CONTRIBUTION TO OUR KNOWLEDGE OF THE CHEMISTRY OF WOOD.

PSEUDOTSUGA TAXIFOLIA AND ITS RESIN.

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T H E S I S

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The fundamental idea in all successful commercial processes is to obtain a marketable product from cheap raw material. In a great many commercial fields, however, cheap raw materials are becoming limited. This means that one of three things must be done: either new materials must be obtained, the source of the original materials conserved, or the present waste products utilized.

One of these sources of supplies which is rapidly decreasing is our forests. If nothing is done in the immediate future toward the conservation of these forests, a substitute for our forest products must be found. The cost of wood has so increased in the past decade that manufacturers have had to practically double the prices of their products in addition to increasing the efficiency of their methods.

The United States Government has recognized these facts and has established a Department of Forest Service. This department has two distinct fields of work; 1st, the conservation of the forests either through governmental measures or though aiding the manufacturers of forest products to carry out their processes with greater efficiency, 2nd, the study of the effect of forests upon climatic and agricultural conditions.

Waste. In no other branch of manufacture has there been such a stupendous waste of valuable material as in the wood industry. When we consider the vast amount of waste in logging, in lumbering, and even in pulping, the facts are astonishing. This is true notwithstanding the fact that modern machinery and economical methods have greatly decreased the waste.

According to recent experiments (J.Ind.Eng.Chem., 3, 4.) and data collected the wood waste is fully sixty per cent. of the original trees. This immense amount is appalling. But this waste is not all. Young trees are broken down and destroyed by falling timber and by forest fires. This waste, according to the Forest Service is far greater than is the waste from the large trees, since it means the total destruction of the forests.

In Bulletin 88 of the Forest Service (Properties and Uses of Douglas Fir) we find a discussion of the waste in this particular species. "The waste from logging and milling Douglas fir and the question of putting this waste to use, has received much attention. Waste begins with the felling of the timber in the woods and continues through the transportation of the logs, particularly if they are carried by water. It is conspicuous at the saw mill, planing mill, manufacturing plants and shops, through the various branches of the building trades, and among the makers and users of railway ties.

"It is claimed that the waste incident to the logging of Douglas fir is often as much as thirty or forty per cent.--that

that much of the tree is actually left in the woods. The top-cut log is likely to be thrown away, because it contains defects which would reduce to low grade the lumber sawed from it. The market for such lumber is poor, and the operator simply leaves the log to decay or to increase the fire menace. In rare instances the tops and branches are cut into cordwood, but nearly always they are left where they fall. The breakage of trees in felling constitutes a large proportion though it is usually unavoidable, since the tree's size and weight, brings it down with great violence, and if the ground is uneven a broken trunk is likely to result. Then, too, smaller trees are broken by the fall of the large trunks, though the practiced feller tries to avoid this.

"When driving is resorted to, many logs are broken in jams, or by impact against rocks or other obstacles. Where splash dams are employed, the waste due to driving is increased by the many logs which are usually left stranded on the banks of the stream and never reach the mill. From 5 to 10 per cent. of the logs may be so wasted. This large item of waste is generally eliminated when the logging is done by rail.

"Slabs and other refuse, if converted into lath and other salable commodities, cannot properly be classed as waste; neither should sawdust and other odds and ends burned for fuel in operating the plant. Some loss is, of course, unavoidable, but the material that goes into the refuse burner is sheer waste. Fortunately, these burners are becoming less numerous, and there is more care

in sorting the stuff that goes into them. However, a number of Douglas-fir mills still operate burners where practically all the mill waste is consumed.

"It is a general rule that the item of waste is reduced in each succeeding stage of manufacture. Therefore, since the lumber which goes to the planing mill has nearly reached its final form, the planing-mill waste is less than that of the saw mill. Planing-mill waste consists chiefly of shavings and trimmings; the former usually goes under the boilers for fuel, and when the latter does not go there also it is usually sold for kindlings.

"The waste in manufacturing varies greatly through a long list, and the waste in one factory is not a sure measure for the waste in others. In practically all wood-using industries the shavings and small pieces which cannot be worked into finished products go as fuel to furnish power for operating the plant. If the factory does not need all the fuel for its own use, a sale is generally found outside.

" A considerable part of the waste chargeable to the building trades is due to the even lengths in which siding, flooring, joists, scantling, and other building materials are sold. Douglas-fir manufacturers have recently agitated the question of making odd lengths, whereby the waste can be reduced, and it now seems probable that both odd and even lengths will be produced in the near future. The waste due to the nonmanufacture of odd lengths in planing-mill products amounts to about 2 per cent. of the total amount so man-

ufactured.

"The waste item in railway ties and other large material is considerable because of the rigid inspection rules. Most Douglas-fir ties are sawed, and the waste is much less than it would be if hewed ties were demanded. The rejected timbers which the inspectors throw out may be sawed into blocks and sold for fuel, and the actual waste is thereby lessened."

Several suggestions are given in the above bulletin for the utilization of waste wood, but these are not sufficient to solve this great problem, neither do they appear to be efficient from a commercial standpoint.

A statement sent out to all interested, by the Forest Service, upon "The Utilization of Waste Wood" will give a larger idea of what is now done with some of the waste. "In converting trees into usable form there is entailed a certain amount of waste, which varies with the form of the product and the value of the work. The difference between loss and waste should be kept in mind. Loss occurs when material is sacrificed because it cannot be used with profit. Waste occurs when only a part of the possible marketable product is used.

"This waste, whether resulting from operations in the woods, at the saw-mill or in the factory, is capable of utilization in two ways. One method is to use it in the form in which it grows; the other, to change its original form. In the first case small wooden articles, such as insulator pins, clothes pins, tool handles,

wooden lath, etc., are made; in the second, the form and substance of the wood is entirely changed by some mechanical or chemical process and such products as wood pulp, charcoal, alcohol, turpentine, rosin, etc., are produced.

"At the present time in this country, in view of the enormous amount of wood available and its relatively low price, the use of waste wood in its original form except as fuel, is not always practical. There are a number of reasons for this. First, there may not be enough waste annually to warrant the installation of the special machinery required; second, the waste may be in innumerable sizes and shapes and the cost of sorting thereby prohibited; third, the manufactured products may be so far away that the freight would absorb the profits; fourth, the waste may have a fuel value equal to, or even greater than, the profits from further manufacture. On the other hand, if the amount of waste is relatively large and the sizes and shapes few in number, and the markets are not too distant, it often happens that small products can be made from larger pieces of waste with very little additional expense. For example, cull maple broom handles become handles for croquet mallets; cull hickory wagon rims are reduced to first-class spokes, cull hickory spokes to hammer handles; white pine edgings are turned into curtain rollers, yellow pine edgings are made into lath; birch and oak trimmings go into picture frames, and so on. The products possible to manufacture in this way are countless and range from the small wooden button of maple to the pyrographical board, two feet square, trimmed from the end of a basswood box

board.

"In the other field of wood waste utilization, however, where the form and substance of the wood are changed and wood pulp and distillation products are made, the outlook is often more promising. In making pulp from yellow pine, for example, the size and shape of the waste is relatively immaterial. The important factors here are the necessary daily volume of waste and a good water supply. In distillation the volume of the waste is also an important factor. In these fields of utility, however, all woods are not suitable. In the vicinity of pulp mills, soft woods like spruce, poplar, aspen, balsam, hemlock, pine, basswood, and tulip poplar can usually be sold to a good advantage. In destructive distillation, beech, birch, and maple are most largely used. Many other woods, however, are coming into use for both of the above purposes."

The following methods of utilizing waste wood are now in use: sawdust flour,as an absorbent for nitroglycerine in the making of dynamite; the extraction of the resinous material from the wood or steam distilling it for the terpenes; the conversion of sawdust into fermentable sugars; and the making of briquettes for fuel. All of the above processes do not utilize everything, each having its own waste. Consequently this only partially solves the problem, and leaves an immense field for both mechanical and chemical investigation.

Since we are little concerned with the working up of the wood in the form in which it grows, but are chiefly concerned with those processes which change the wood into other substances, that is, change its original form and structure, we will consider only the latter . Among these are the following: the destructive distillation of the wood, making it into paper pulp, steam distillation to obtain the terpenes and resins and then pulping, and the converting of wood into fermentable sugars for the manufacture of alcohol.

Destructive Distillation. As has already been stated above, the hard woods such as beech, birch and maple, are the most suitable for destructive distillation. However, other woods have been used. That the destructive distillation of Douglas Fir is commercially possible is shown by the following extract from Bulletin 88 of the Forest Service:

"Several distillation plants operate in the Douglas-fir belt west of the Cascades in Washington and Oregon, and depend entirely on the waste at nearby saw mills for their wood supply. Only the pitchy wood is used for the distillation of the regular run of fir is not commercially profitable at the present time. Pitchy wood is unsuited to the manufacture of lumber, and would be often a total loss if not taken by the distillation plants. It is carefully selected from the scrap piles at the mills, and the price varies with the quantity of the pitch. The operations are said to be profitable, and will undoubtedly be much extended as better processes and markets are developed."

The process is carried out in specially constructed retorts, to use both steam and destructive distillation. The steam distillation is commenced after charging with the wood chipped in the blocks six inches long by two inches in cross section. The temperature is gradually raised, during six to eight hours, to about 325° F. at which point practically all the turpentine has passed over to the condensers. From here it is run off and refined. As soon as the oils begin to distill over into the condensers, as shown by the distillate run off, the steam is turned off and the dry distillation process is begun. It is continued about thirty-two hours, the temperature being gradually raised to 832° F. Between 350° F. and 600° F. pyroligenous acid and tar oils pass over in the form of vapor, are condensed, drawn off, and mechanically separated, the acid being the heavier. Between 600° F. and 800° F. pyroligenous acid, tar vapors, and wood gas pass over into the condensers. At 832° F. only charcoal remains. The commercial products of the distillation are turpentine, pyroligneous acid, tar oil, tar, pitch, and charcoal.

A cord of selected Douglas-fir saw-mill waste at one of the commercial distillation plants in Oregon gave the following yield of distillation products:

Pyroligneous acid	gallons	150
Tar oils	"	12
Tar	"	20
Charcoal	pounds	800
Turpentine	gallons	4 to 12
Pitch	pounds	200 to 400

Experiments made by the forest service on Douglas-fir stumpwood, using a small steam distillation apparatus, showed for different samples of wood a variation of from 60 gallons of turpentine per cord to none at all. Other samples from the same stump varied from 5 to 40 gallons per cord, the former yield being obtained more usually. The average yield per cord from stump wood is given as :

Turpentine	gallons	8
Tar oils	"	20
Tar	"	35
Charcoal	bushels	42

The conclusion of this bulletin is as follows:

"The average run of fir is not a profitable wood for distillation at this time, but it may become so when the demand for charcoal, turpentine and other important by-products increases."

Wood Pulp.- The paper industry like the soap and glass industries was one of the first to be developed. It had its beginning long before the Christian Era, when the Egyptians made a writing material from papyrus. The making of paper from fibrous material appears to have been carried on by the Chinese at least as early as the second century B.C. In 1751 the Arabians obtained the art from Chinese whom they had captured. Investigations have shown that the Arabians used flax as a raw material for paper making, but their method of treatment is unknown. The first mention of paper made from rags appears in a tract by Peter, Abbot of Cluny (A.D.1122-1150), adversus Judaeos, cap.5, in which he refers to books written on material made "ex rasuris veterum pannorum". (Encyclopaedia Brit.11th Ed.,725). Although there are records of paper having been made from many fibrous materials, rags were the only material employed until the middle of the 19th century, when wood was introduced. Rags are used to-day for some of the best grades of paper. However, most paper is made from wood or grasses, such as esparto.

The great wood pulp industry dates back to the first of the 19th century. The making of chemical pulp, that is, pulp by strictly chemical processes, which is the only kind that will be considered here, was first attempted by Koops in 1800(Cross and Bevan: "Wood Pulp and its Uses",90). He boiled straw and later wood, with a crude soda lye in an attempt to obtain a substitute for rags. In the years following these experiments, several

chemicals suitable for reducing fibrous materials to pulp were introduced into the manufacturing world, thereby increasing the possibilities for reducing wood to pulp. These led to the development of several different processes of wood disintegration known as the Sulphite, the Sulphide, the Sulphate, and the Alkali or Caustic Soda processes.

Sulphite Process.- The sulphite wood cellulose process, although not as old as the alkali process, is the most important to-day, more chemical wood pulp being made by it than by any other process. Essentially it consists in subjecting wood to the action of sulphurous acid and its acid salts in closed vessels at high pressure for definite periods of time. By varying the conditions, that is, the strength of the liquor, the steam pressure, and the length of time taken for digesting, products of almost any desired quality may be obtained.

In carrying out the process on a commercial scale there are two chief methods: the Quick Cook Process and the Slow Cook Process. The first consists in digesting the wood at a high pressure of 80 to 100 pounds to the square inch for six to ten hours, while the temperature sometimes reaches as high as 176.5 C. If strong liquors are used a strong pulp of good color is obtained, which bleaches readily. But if dilute or weak liquors are used a reddish pulp is obtained which is not easily bleached, but which is very strong and tough.

In the Slow Cook Process the pressure seldom exceeds fifteen pounds, while the boiling is continued for 30 to 72 hours. This process produces the strongest fiber we have and uses a weaker solution for digestion than the Quick Cook Process.

In discussing the wood cellulose industry in Scandinavia (J.Soc.Chem.Ind., 15, 249.)J. Beveridge describes the bisulphite process as using bisulphites of lime, sodium and magnesium, most generally using the bisulphite of lime. Out of a total of 100 parts of SO_2 in the liquor 34 parts are combined and 66 parts are free, the total contents being four to five per cent. of SO_2 in the solution. For pressures above 100 pounds the cooking is carried on for five hours.

B. C. Tilghmann, an American chemist, was the first to suggest the use of a solution of sulphurous acid gas, or a solution of its salts, as a suitable liquor for breaking down wood into pulp. Experiments were carried on by him in 1863,and in 1866 he was granted a patent (English Patent 2924) for the manufacture of pulp from wood by treatment with a solution of sulphurous acid and calcium bisulphite.

The following is a part of the claim of Tilghmann's first United States Patent, as given in the Patent Office Report(2nd Sess. 40th Congress II,1303. U.S.Pat.70485).

"The process of treating vegetable substances which contain fibers with a solution of sulphurous acid in water, either with or without the addition of sulphites or other salts of equivalent chemical properties, as above explained, heated in a closed vessel, under

pressure to a temperature sufficient to cause it to dissolve the intercellular incrusting or cementing constituents of said vegetable substances, so as to leave the undissolved product in a fibrous state suitable for the manufacture of paper, paper pulp, cellulose, or fibers, or for other purposes, according to the nature of the material employed.

.....

"Also, the recovery and re-use of sulphurous acid and sulphite from the acid liquids which had been digested on the vegetable substances, by boiling said liquids, or neutralizing them with hydrate of lime".

The next work of note was done by Dr. Richard Mitscherlich. His process(Dingl.Polyt.J.1876, 220,564.)was to heat wood for one hour in copper or zinc kettles at three atmospheres pressure and at 110° C., with a solution of calcium bisulphite to which had been added some gypsum, and afterwards hydrochloric acid.

Lioud (Fr.Pat.116996,1877.) cooked wood with a solution of sulphurous acid alone, or combined with a base.

R. Mitscherlich(D.R.P.Kl.55,4179,1878.) treated wood under pressure with a solution of calcium bisulphite or (J.Soc.Chem.Ind. 1,380.)a solution of sulphurous acid, but preferably a solution of calcium bisulphite.

D. V. Francke (Papierzeitung 1883,357 Patents 10/13/81 and 12/21/81.) used four to five degree Baume solution of sulphites of calcium, magnesium and sodium, heating for 12 to 15 hours at four to five atmospheres pressure.

Mitscherlich (Moniteur Scientifique, Quesneville, 5 - 1883: Chem. News 47,280.) treated wood with calcium sulphite solution under pressure. The cellulose was then separated from the soluble materials by filter presses, washed, and made into paper.

The same year G. Archbold published an article (Ber.16,350; J.Soc.Chem.Ind.2,295.) on the preparation of paper pulp on a large scale. The material was macerated for 12 hours with dilute milk of lime, and the mass, after being placed in a digester, was saturated with SO_2 under a pressure of four atmospheres,which effects a complete disintegration of the mass in one or two hours. The product of this treatment was washed, and treated under pressure with three per cent. calcium chloride and .5 per cent. aluminium sulphate dissolved in a small quanitity of water. These salts are finally removed by washing. The product obtained in this way is claimed to resemble cotton wool in appearance. He obtained an American patent (U.S. Pat. 274250.) for the process, using one per cent. milk of lime, one per cent. calcium nitrate, and passing in sulphurous acid, thereby forming calcium sulphite. The mass was then heated at four to five atmospheres pressure.

J. A. Graham(Ding.Polyt.J.253, 323.Eng.Pat.5365,1882.) proposed to use the monosulphites of potassium, sodium, magnesium, etc., to eliminate the chief difficulty of the sulphite boiling process, namely, the evolution of sulphur dioxide. In order to accomplish this, the solution of a monosulphite or of a combination of all of them was introduced into the boiler, and when the gases from the wood were driven off, sulphurous acid in the gaseous or

liquid state was injected. The acid might be injected alone or in combination with potassium, sodium or magnesium. An excess of the acid was employed but not sufficient to form acid sulphites.

R.P. Pictet and G. L. Brelaz (Ding. Polyt.J. 253, 323. Ger. Pat. 26331, 1883.) condemned the sulphite process, because the high temperatures (120°-140°) there obtained, convert the gummy and resinous material into tarry products. By employing an aqueous solution of sulphurous anhydride, 100 to 150 grams of the anhydride in a liter of water, the disintegration may be effected at low temperatures, 80° to 90°.

Ekman (Dingl.Polyt.J. 249, 23.) recommended the use of a solution of magnesium sulphite.

A. Mitscherlich (Dingl.Polyt.J. 251, 262.Am.Pat, 284319,1883.) removed the bark of the wood, which was then cut into small pieces, boiled and passed through a stamping mill, where the fibers were separated and the incrusting material washed out. Before boiling the chips are treated with steam to drive out the gases in the woods and prepare it for the action of the acid. The liquor used for the boiling was a solution of sulphite of lime, there being a definite ratio between the amount of it and of the wood. The first stage was a slow action, and was found to be carried on best at 108° C. The second stage was more energetic, a temperature of 118° C. being attained. On boiling off the sulphur dioxide, the same effect was attained as by reducing the temperature.

(Error in paging.Nos.)
(17 and 18 missing.)

W. Flodquist (Papier Zeitung 1884, 1436.) obtained the liquors for digestion of the wood, by passing SO_2 over moist bones, freed from fats, and so produced a solution bisulphite and phosphate of lime. He used a five degree Baume solution and boiled eight to nine hours, the final pressure being 70 pounds.

D. K. Francke (Ger.Pat.24924. U.S. Pat. 295868, 1884.) heated wood at 150° with a 45° Baume solution of acid calcium sulphite, using 900 to 1250 liters of the solutionto 1000 kilos of wood.

A. Albutt (Eng.Pat 16186.) heated wood to a temperature of 150° C. with a solution obtained by the action of sulphurous acid upon magnesite and dolomite, either together or singly.

W. Schacht (Papier Zeitung 26, 84, 3143.) obtained liquor for digestion wood by nearly saturating with SO_2 the crude recovered soda solution, and then causticising the residual carbonate. The liquor, consequently, consisted of a mixture of sodium sulphite, sodium thiosulphate and sodium hydroxide. The latter is present to deal with the silicates and alumina which exist in the wood, and should not be in excess of the amount required for this. This is claimed to avoid the bad odor of the sulphite mills,and to increase the yield 15 to 20 per cent., and to give better cellulose.

V.Drewsen (U.S. Pat.730439, 1903.) submitted the wood to a preliminary soaking in a water solution of a monosulphite, as magnesium sulphite, long enough to enable to solution to permeate the wood.

R.Eichmann (Ger.Pat.184991, 1906.) subjected wood to the action of sulphur dioxide, and then boiled in the usual manner with sulphite liquors. He claimed to have obtained a larger yield and better quality,in shorter time.

Out of these numerous patents and suggestions has developed our present sulphite pulp process which was briefly stated above. The chief objections to this process are the bad odor, the corrosion of the boilers, and the complete loss of the disintegrating materials.

Sulphite Waste Liquors.- The waste liquors from the sulphite process are at present thrown away in most mills. Although a great many experiments have been made to recover the by-products, no system has yet been introduced for the recovery of the sulphur in a profitable manner, or for the manufacture of marketable by-products.

S.Ferencze (Papier Zeitung 1897, 22, 100, 3575; 102, 3647; 103, 3679.) by analyzing fresh and waste liquors from the Papier und Zellstoff Fabrick. at Unterkochen und Wolfach, obtained the following results: -

Fresh liquor	Total SO_2	3.20	per cent.
	Free SO_2	1.76	" "
	SO_2 combined with Ca	1.44	" "
Waste liquor	Water at 105° C.	88.7	" "
	Organic Material	9.7	" "
	Mineral Ash	1.6	" "
	Sp. G. at 17.5° C.	1.0545	
Mineral Ash	$CaSO_4$=	0.24	" "
	$CaSO_3$	0.94	" "
	$MgSO_3$	0.24	" "
	MgO combined with organic acids	.13	" "
	SiO_2,Al_2O_3,Fe_2O_3,etc.	0.50	" "

H.Seidel (Mitt. d.k.k. Tech.Gew.Muss.N.F. 7, 119-225.)working on liquor obtained from a "Silesian" mill, using the Ritter-Kellner Process, obtained the following results: Sp.G. 1.050; total solids, or residue per 100 cc. dried at 100°, 12.013 grams, that is, 11.44 per cent., containing 9.54 per cent. total sulphur.

Calculated in per cent. in the liquid,

sulphur in the dry residue	1.0910	grams
sulphur as free SO_2	.0320	"
sulphur as SO_3	.0074	"

93 per cent. of the total sulphur was found to be in organic compounds. The potassium content was one gram K_2O per 52 liters.

The principal constituent of these waste liquors is the calcium salt of lignone-sulphonic acid, a true sulphonic acid, with the SO_3H group combined with carbon (Lindsay and Tollens, Ann.267, 341; H. Seidel , Zeit.angew.Chem. 38, 951-956). This salt results from the specific interaction of the bisulphites with the aldehydic or quinonic complex of the wood or ligno-cellulose.

H. Krause (Chem. Ind. 26, 217-227.) gives a comparison of the lyes of the Mitscherlich and the Ritter-Kellner processes. The chief constituent is the calcium salt of lignin-sulphonic acid, but the latter is darker and contains more sugar. The sugars are separated by evaporating the liquors in the presence of barium carbonate to a pasty consistency, mixing with sand and extracting three to six times by exhaustion with hot 90 per cent. alcohol. It was found that wood obtained in the autumn contained more sugars than that obtained in the spring. The following is

the analysis for sugars and allied compounds from each liquor:

	Mitscherlich per cent.	Ritter-Kellner per cent.
Furfural	0.01	0.02
Pentosans	0.40	0.29
Hexosans	0.21	0.49
Total Sugars	1.48	1.47
Pentose	0.47	0.41
Mannose	0.48	0.48
Levulose	0.28	0.25
Galactose	0.01	0.01
Dextrose	-----	trace

No work of value was done upon these waste liquors until about thirty-five years ago, but the number of patents that have been obtained and the variety of suggestions that have been made within that time are sufficient evidence of the importance of the problem.

Cross and Bevan (Eng.Pat.1548, 1883, J.Soc.Chem.Ind. 2, 541.) found that if they acidified the waste liquor, and then added gelatine or albumin, a peculiar substance was obtained, to which they gave the name lignosine. If they precipitated it by gelatine, they called it gela-lignosine; if by albumin, albu-lignosine. This substance was found to be suitable for use as size, as a mordant and as a vehicle for colors and pigments.

A.Frank (Eng.Pat.13286, 1886.) proposed to use for forage and manure the waste remaining ~~after remaining~~ after removing the free and combined sulphurous acid from the liquor. This was precipitated as calcium mono-sulphite, ~~and~~ separated by filtration, and washed by elutriation with water containing sodium and calcium chlorides. This calcium mono-sulphite was worked up for fresh sulphite solutions by one of the following methods:--

first, stirred in an aqueous solution of sulphurous acid; second, treated with dilute sulphuric acid, forming calcium sulphate and free sulphurous acid which changed the undecomposed mono-sulphite into bisulphite of the desired composition; third, the mono-sulphite was introduced into a solution of sodium acid sulphate, precipitating calcium sulphate and forming a solution of calcium bisulphite. The above solution, after precipitation and removal of the mono-sulphite, was treated with air and carbon dioxide, and evaporated.

Lindsay and Tollens carried out some extensive researches on the waste liquors from the sulphite process (Ann.267,341-366). In the liquors they detected dextrose, galactose, galactan, mannose, pentoses, vanillin and allied substances, and fermentable carbohydrates.

V. B. Drewsen (Eng.Pat.2629, 2/10/92) treated the waste liquors from the sulphite process with caustic lime at 90 pounds pressure, in a closed vessel. The organic sulphur compounds and calcium sulphite are precipitated, filtered off, and the calcium sulphite and lime compounds used for the production of the bisulphite.

E. Bruck (Chem.Zeit. 95, 1782.) treated the waste liquors from this process with gelatine and alum for removal of the soluble lignone derivatives, and finally with chalk to neutralize the acid. This treatment he claims removes one-fourth of the dissolved matter, and a large proportion of the uncombined sulphites, and gives an effluent which remains unchanged for months.

A. Mitscherlich (Eng.Pat. 12927, Ger. Pat.72161.) separated the constituents of the waste lyes of the sulphite process by Osmose in a special apparatus, and utilized such constituents for a tanning material and a cementitious material. He also obtained alcohol by treatment of certain parts of the liquor, and further obtained food for animals. He later obtained a German Patent (72362) for the production of combining materials suitable for binding in briquettes.

C.D. Ekman (Papier Zeitung 69, 2218, Ger.Pat.81643.) obtained a substance he called "dextrine" by evaporating the neutralized liquor to 34° B. and then at 85° C. adding suitable salts, as magnesium sulphate, whereby the dextrine separated out and floated on top. It was dried, packed and used in textile manufacture.

P. Remy (Papier Zeitung 22, 13, 426.) treated the lyes with iron or lead salts in quantities equivalent to the calcium salts, when a waterproofing solution was obtained. Iron salts gave more satisfactory results.

Franz Müllner(Papier Zeitung 23, 19, 687, Austrian Pat.) recovered by-products from the waste liquors of the sulphite mills by evaporating the liquor, adding an amount of lime corresponding to the amount of sulphur compound in solution;-then adding bauxite or some aluminium salt, and injecting sulphur dioxide. The aluminium was precipitated as the hydroxide. This was used for aluminium salts or treated with sulphuric acid and used for sizing.

The work upon sulphite waste liquors up to 1900 has been summarized by H. Seigel (Zeit.angew. Chem.38, 951-956.). He states that several attempts have been made to recover the sulphur by some modification of Chance's process, but the sulphur dioxide is too dilute and the calcium sulphide is impure. Many sulphur recovery processes are based on the false assumption that the sulphur is largely present as free sulphur or combined with sulphites, whereas it is practically all in organic compounds. Drewson's process of recovery by heating of lime under pressure is practical, but the bisulphite produced from the sulphide obtained is not sufficiently pure, and the manipulation is expensive. As a manure, the low percentage of potash and nitrogen and the gummy nature of the solid material are disadvantages. The employment of wood liquor with cattle fodder has been proposed, but it is out of the question on account of the six to eight per cent. of sulphur. The dry distillation of the liquor gives useful products and good carbon, but the concentrating of the liquor is too expensive. For the manufacture of oxalic acid it cannot possibly compete with sawdust. A large outlay has been expended in trying to utilize the liquor for the tanning of hides, but although hide powder will absorb 28 per cent. of the dry substance, no suitable leather has been obtained. As an adhesive the concentrated liquor may find a limited application, as also for the manufacture of briquettes, and in the petroleum industry. Mitscherlich has patented a paper size, prepared by boiling wood liquor with glue, rosin and soda. In the dyeing industry, as a substitute for dextrin, the

reducing properties of the liquor have rendered the colors somewhat fugitive. Wood liquor may replace zinc dust and glucose in the indigo vat. Finally, under the manufacture of "lignorosin" these liquors have been employed in wool mordanting for the reduction of chromic acid (J.Soc.Chem.Ind. 17, 844.).

T. Knösel (Chem.Zeit. 26, 2. 229.Ger. Pat. 128213.) proposed to use the waste as a fertilizer by evaporating to 25° Baume and then mixing with approximately an equal weight of Thomas slag meal. He found that when these were mixed there was a reaction, heat was liberated, and a brownish-yellow, solid mass was obtained. Practically all the phosphorous was found to be in the citrate soluble form, while only 75 per cent. was in that form in Thomas slag. The alkalinity of the meal was neutralized by the sulphurous and lignin-sulphonic acid.

E. Trainer (Ger.Pat.181126, 1905.) evaporated the liquors, dried them, and with the addition of compounds of the alkalies and alkaline earths, finally divided lignite and low grade coal, formed briquettes and carbonized them. He also obtained a patent (Ger.Pat.197195, 1906.) for a process for rendering insoluble in water the soluble organic constituents contained in the sulphite cellulose lyes. These were heated with hydrochloric acid, and finally,under pressure with the addition of aldehydes, as formaldehyde, yielding a gelatinous mass indifferent to all known solvents, as well as alkalies and acids, and therefore applicable in the manufacture of insulating materials, roofing, felt, artificial leather, floors, wood pavement, and artificial asphalt.

Kumpfmiller (D.P.183415, 1905.) obtained a tannin, and above all a saturated extract for tanning leather, as well as a dye, by freeing the liquor of sulphurous acid without the addition of basic salt, but by heating. The calcium monosulphite was precipitated and the rest of the combined lime was removed by the addition of an organic acid, forming an insoluble calcium salt.

P. Klason (Papierfabr. 7, 26-31, 627-629, 671-672, 701-702, 795-800.) would discharge the lyes continuously and regularly into rivers after cooling and aërating.

W. Haage (Eng.Pat.6631, 1910.) used the evaporated waste lyes as a binding material in the manufacture of fuel and ore briquettes, building blocks, and the like.

A Nicolle,(Fr.Pat.425991, 1910.) in using the residue from the evaporation of the waste lyes as an agglomerate and as a binding material in briquettes and the like, evaporated the lyes to a thick syrup only, and then mixed with them, salts of chromium, iron, cerium, and others of this group. These aided in withstanding weathering.

M. Hönig (Fr.Pat.413849, 1910.)prepared a tanning extract from the lyes by adding the calculated quantity of sulphuric acid necessary to decompose the esters and salts of sulphurous acids present, and to partly liberate the sulphonic acid of lignin from its calcium salts. The solution was then filtered through tanning material to remove iron,then concentrated.

Matheus (Papierfabr. 9,1435.)obtained a decolorizing charcoal from the waste lyes, by boiling off the sulphur dioxide, neutralizing with lime, evaporating the liquid thus obtained until it swelled and hardened. It was then powdered and subjected to destructive distillation. A very porous charcoal, and a good substitute for bone charcoal was obtained. The distillate resembled the distillate obtained from wood.

J. H. Vogel (Papier Zeit. 35, 1547.) states that the different sulphite mill wastes should be treated as follows: - 1st, the cooking liquor evaporated, mixed with coal and burned; 2nd, the remaining waste settled in outside basins and then filtered sufficiently well so that it can be reused in the mill; 3rd, some wastes may be used for irrigation; 4th, the white water waste purified by sedimentation in baffled settling basins.

Hilding(Papierfabr. 9 Fest u, Austandshift 81-82.) describes a pine oil obtained from the waste liquors. In the digestion of pine wood by the sulphite process a soap is skinned off the surface of the black liquor, and when decomposed by acids, yields a thick oil. This is recovered at certain Swedish pulp mills under the name of "fluid resin" or "Taloel". After being purified by washing, the oil deposited a copious mass of crystals. The oil was distilled at reduced pressure, and when treated by Twitchell's method, indicated 53.1 per cent. fatty acid, and 46.9 per cent. resin acids. It was free from phenolic constituents. The oily portion of the distillate was separated from the crystallized resin acid by pressure, and fractionally distilled at fifteen

millimeters pressure. Oleic and linolenic acids were identified in the distillate. The author believed the fatty acids to exist in the wood in the form of glycerides, and glycerol was found in the ether-alcohol extract of sap-wood. The resin acid was purified by washing with petroleum, and crystallized from alcohol. The product was a mixture, melting at 156° to 180°, dextrorotatory and having an acid value of 186.4.

Among the few practical processes for the utilization of the waste sulphite lyes is the fermentation of the same, after proper treatment, for the manufacture of alcohol.

G. Ekström (Papierfabr. 8,582.) tells of a plant erected for the manufacture of alcohol from the lyes, by neutralizing with the waste causticization sludge from the sulphite-cellulose mills, and then fermenting. From the first, the output was about 50,000 liters per month. The results led to the enlarging of the plant, making it possible to quadruple the production. This process is identical to that of Lindsay and Tollens, except that they used lime to neutralize the lyes.

He also obtained patents (U.S.Pat.1,042,332, 1912; Eng.Pat. 6741, 1910.) for the treatment of the lyes with calcium carbonate (or similar materials) and ammonium sulphate, and then fermenting.

C. G. Schwalbe (Z.angew.Chem.23, 1537.) explains a similar process, neutralizing with lime for waste causticization sludge.

The total production of this grade of alcohol in Sweden in 1908-9 was about 22,000,000 liters (absolute),(Chem.Zeit. 34, 1077.). If the process was extended to all Swedish sulphite works

the annual output would be about 3,500,000 gallons, while 800,000 gallons could be produced in Germany (U.S.Cons.Rep. Nov.1911). However, the laws in these countries are so stringent that the development of the process is slow. Since the alcohol from the waste sulphite lyes is of the nature of denatured spirit, owing to its impurities, its application is limited.

Sulphide Process.- Another process that is used in the manufacture of paper pulp from wood is the sulphide process, in which a solution of alkali sulphide is used to disintegrate the wood.

Der Oesterreichische Verein für Chemische und Metallurgische Production were the first to use this method. They patented a process (Ger.Pat.25485, 1882.) which consisted in digesting wood with a solution of sodium sulphide of 10° Baume,- thirty parts of the pure sulphide to one hundred parts of wood,- at a pressure of five to ten atmospheres for six to ten hours.

Blitz (Dingl.Polyt.J. 252, 323-328.) boiled wood three or four hours in a closed vessel at a pressure of four atmospheres, using a solution which contained six kilos of sodium sulphide, three kilos of sodium hydroxide and one gram of ammonium vanadate.

A. J. Boult (Eng.Pat.18018, 1890.) boiled wood with a mixture of the sulphides of calcium, barium, strontium and magnesium in water. The boiling was continued from one to ten hours at two to ten atmospheres pressure, the amount of sulphides, the pressure and time of cooking varying with the nature of the material used. The sulphides might be mixed with carbonates or hydroxides of the alkalies. He claimed the treatment would remove incrusting materials but not destroy the length and firmness of the fiber.

The Oesterreichische Verein für Chemische und Metallurgische Production were also the first to utilize their waste(Ger.Pat. 31747, 1884). They evaporated the waste liquor from their sulphide process,

and furnaced with lime and coal to a black ash. By boiling this black ash with water the sodium sulphide lye is obtained, or it may be regenerated by heating the dilute waste lyes under a pressure of about three atmospheres.

H. Falk (Papierfabr. 7, 469-472.) obtained the following substances by the condensation of the volatile by-products in the manufacture of wood pulp by the sulphide process, the yields being calculated per ton of cellulose obtained from pine wood:-

	In Oil	In Water
Mercaptan	0.062 K.	0.06 K.
Dimethyl sulphide	0.927 K.	0.17 K.
Dimethyl disulphide	0.103 K.	0.05 K.
Oil of Turpentine	8.487 K.	0.92 K.
Distillation residue	0.721 K.	-----
Methyl alcohol	-------	5.0 K.
Ammonia	-------	0.18 K.

A good grade of pulp is obtained by this process, but the odors liberated are very offensive, the gases are injurious to vegetation, and the liquors have a very corrosive action on the boilers. On account of these objections this process is little used.

Sulphate Process.- In discussing "the Wood Cellulose Industry of Scandinavia" (J.Soc.Chem.Ind. 15, 249.) James Beveridge states that the sulphate method is really not a sulphate method at all, but a combination of the caustic soda and the sulphide processes. Salt cake is employed to yield the sulphide. It is added to the black carbonaceous mass in a calcining furnace during the soda recovery process. The supply of air present is limited and sodium sulphide is formed. The ash is causticized in the usual way before using in the digesters.

The great objections to this process are that it requires more sodium salts than the caustic soda process per unit weight of pulp, and the presence of the sulphide makes greater wear and tear on the evaporators and furnaces.

In 1882 Carl D. Ekman obtained a patent (Eng.Pat.3062.) on a process for the reduction of wood to pulp by treatment with magnesia and sulphuric acid. He boiled the wood, by means of a steam jacket, in a mixture of 14 parts of magnesia, 44 parts of sulphuric acid and 942 parts of water. The pressure was raised gradually for seven hours to about 90 pounds to the square inch. The mass was allowed to stand for one to three hours, when the liquor was drawn off. He states that the gummy material extracted can be used as a substitute for dextrine.

Dahl (Dingl.Polyt.J. 276, 411.) used a solution of 16 parts sodium sulphate, 50 parts of sodium carbonate, 20 parts of sodium hydroxide, and 10 parts of sodium sulphide. For every 100 kilos of wood, 26 kilos of this salt mixture was used. The salt solution

varied from six to fourteen degrees Baume, while a pressure of five to ten atmospheres was maintained for three to four hours, steam being used as a source of heat.

W. P. Thompson was granted an English Patent (13004, 1887) for boiling wood with a solution of the hydroxide, sulphide and sulphate of soda. The soda was recovered by evaporation and calcining. To replace the lost soda, fresh sodium sulphate was added to the liquid before evaporation. The calcining reduced the sulphate to sulphide, therefore the mass was mostly sodium carbonate and sulphide. The mass was causticized in the usual way with lime. This is the manner in which the sulphate process is now carried out.

In working on the possible by-products from a wood pulp mill, using the sulphate process with digesters running under ten atmospheres pressure, H. Bergström and O. Fagerlind (Papier Zeit.33, 3779,) condensed many substances in the vapors discharged from the digesters. They obtained eight kilos of oil of turpentine from pine wood, one kilo from spruce; five kilos of methyl alcohol, one kilo methyl mercaptan, three kilos of dimethyl sulphide, one-tenth kilo dimethyl disulphide, and two-tenths kilos ammonia. All were calculated per ton of finished cellulose. They also noticed hydrogen sulphide, carbon dioxide, acetone, and two other unidentified bodies.

P. Klason (Papier Zeit. 33, 3779) obtained,as a by-product from the sulphate process, five kilos of turpentine oil per ton of pine wood. A better grade of oil was obtained by purifying as soon as distilled, thereby avoiding the formation of dimethyl disulphide, which is formed if the liquors are allowed to stand.

Since the sulphate process is of very little importance on account of the objections stated above, little work has been done upon it, or upon its waste liquors. However, in the development of the chemical pulping processes it will probably be modified, and come to be one of the most important, because it yields a high percentage of good grade pulp.

Special Processes.- Several other methods for the making of wood pulp, besides those discussed above, have been suggested and patented. The most important are briefly stated below.

Barre and Blondell (Chem.News 4, 213.) disintegrated wood with nitric acid, first saturating the wood with water. The acid was finally neutralized with sodium carbonate, and the nitric acid recovered.

Another method (Ill.Öst Pat. Bl. Bd. 5, 79; Die Chem.Ind. 6, 340.) was to heat the material, wood, straw, jute, etc. with ammonium hydroxide of 0.9 Sp.G., with or without pressure for four to six hours.

Young and Pettigrew were granted patents (Eng.Pat.14735, 1884; N.Amer. Pat. 322822.) for the manufacture of paper from wood by treatment with a solution of nitrous or nitric acid, finally neutralizing the liquor with alkali and recovering the acid.

C. Kellner (Eng.Pat.15942.) obtained pure cellulose by treating wood placed in two cylinders, connected by pipes, with a sodium chloride or other chloride solution. The cylinders are heated with steam coils to 126°, and a current is then passed through the solution, the direction of the flow of the current being changed from time to

time. He simplified this process in English Patent 5422, of 1900.

Payen reports (Dingl.Polyt.J. 276, 411.) from a cellulose factory making paper from wood, five millimeters thick, by first treating with warm aqua regia, and then heating with alkalies.

Barchet and Marchard (Dingl. Polyt.J. 276, 411.) heated wood with hydrochloric acid for twelve hours and then treated with sodium hydroxide to neutralize the acid.

Kellner (Eng.Pat.24287, 1893.) dampened the wood, and then exposed it to the action of nitric oxide, nitrous, hyponitrous, hydrochloric and chlorous acids, after which he treated it with water and subjected it to mechanical treatment. The material was finally treated with alkalies to dissolve out the by-products.

Cross (Eng.Pat. 409, 1894) treated one part of wood with three parts of ten per cent. nitric acid solution, and heated to 80° C. After pressing to remove the spent liquors, he heated the material with a solution of soda ash.

Oriole (Prakt. Handb. der Papierfabr. 42, 1631-32.) found that both hydrochloric and nitric acids penetrated wood and removed the encrusting material, but hydrochloric blackened while nitric did not. A solution of 20 per cent. nitric and 80 per cent, hydrochloric did not blacken. He found that 100 parts of wood yielded 50 parts of long, strong fiber when treated with 40 per cent, of the above solution, and then bleached.

Lifschütz (Ger.Pat. 60233.) treated wood with a cold mixture of three parts of nitric acid to one of sulphuric. The wood was finally washed with water and sodium hydroxide. He obtained a yield of 45

per cent. cellulose. The acid was reused until the nitric acid was exhausted, when it was practically saturated with oxalic acid, which crystallized out, The sulphuric acid was reused with fresh nitric acid.

Nodon , Bretonneau and D'Alton-Shie (Rev.Prod. Chim. 1, 13 , 196.) steeped the raw material for several hours in a weak caustic soda solution containing sulphide or silicate of an alkali or alkali earth, and then subjected to electrolysis in an improved conical vat. using a low voltage.

H. Tauss (Chem. Ind. 12, 514.) discusses the possibility of obtaining paper by treatment of wood with distilled water under pressure at a high temperature.

Buehler (Chem.Ind. 26, 138.) reported that at temperatures above 150° centigrade, phenols dissolve the incrusting materials, resins, and lignin of wood and liberate cellulose. Wood tar oil of high phenol and cresol content proved to be very good.

Bergerhoff (Nr.163070, Kl. 55 b. 1904.) heated wood under pressure with water, in order to retain the bright color. He heated at 125° C. and five atmospheres pressure for six to eight hours.

C. G. Schwalde (Ger. Pat. 204460, 1907.) treated finely ground wood with gases containing oxides of nitrogen until these were no longer absorbed. It was allowed to stand about three hours, and then treated with two per cent. sodium hydroxide solution. On boiling, the wood disintegrated rapidly to fibrous pulp.

As far as is known, no one of these patents or suggestions has been put into practical application upon a commercial scale.

Caustic Alkali Process.- Although the caustic alkali process for the manufacture of cellulose from wood was the first to be developed, the discussion of it has been reserved until now, since most of the work done by the author was upon this process.

Since the caustic alkalies will disintegrate fibrous material readily, even without heat or increased pressure, when sufficiently concentrated, it was most natural that this should be the first process developed.

The alkali treatment of wood for the manufacture of wood pulp consists in heating the wood, in the form of small chips, in large digesters, with a solution of caustic soda of about 20° Twaddell. The pressure is raised 100 to 150 pounds to the square inch where it is maintained for six to eight hours. However, the conditions are varied according to the nature of the work and of the pulp desired.

According to an article appearing in the Papier Zeitung (J.Soc. Chem.Ind. 10, 786.) the process of treatment consists in heating the charge of wood and alkali with direct steam in revolving boilers at a pressure of 125 pounds for one to two hours, depending on the timber, using 75 kilos of sodium oxide per cubic meter of wood.

In Scandinavia (J.Soc.Chem.Ind.15, 249.) the wood is digested for five to six hours at a pressure of 110 pounds, in lye containing five per cent. Na_2O. The total time for one digestion is about ten hours.

The first patent known for this process, and apparently overlooked by most writers along this line, probably because it was not developed, was one issued by the United States, upon August 3rd, 1830, to L. Wooster and J. E. Holmes (Reg.of Arts.and Sc. 1831; Dingl.Polyt.J. 44, 316.) for a new method for manufacturing paper and pasteboard from wood. The wood was first made into shavings and then covered with boiling water and twelve to eighteen pounds of vegetable or mineral alkalies per 100 pounds of wood.

The next important patent was issued to Watt and Burgess (U.S. Pat. 11343, 1854.). The wood was reduced to shavings and then boiled in a solution of caustic soda, the time of boiling and the strength of the solution depending upon the nature of the wood. It was then washed, pressed, and exposed to the action of chlorine, or any compound of chlorine and oxygen, either gaseous or aqueous; washed and pressed again, occasionally using mechanical aid. It was then placed in a weak solution of caustic alkali, when it assumed the form of a brown pulp. This was washed, and after freeing from alkalies, was bleached.

C.M. Rosenhain (Dingl.Polyt.J. 220, 81-87.) states that this process was first used in 1865 in the mills of Jesop and More at Monajunk, near Philadelphia, but H. Tauss (Ibid. 251; 411.) states that it was started by the Manayank Wood Pulp Works Co. of Philadelphia in 1854. The twelfth United States Census (1900, 9, 1023.) states the first wood pulp was made in the United States in 1854, thus corroborating the statement of Tauss.

Rosenhain states, however, that on account of the want of suitable machinery and apparatus the quality and price of the product did not

come up to requirements. These difficulties were soon remedied, and in 1868 a Gloucestershire paper company in Cone Mills, near Sidney, erected a large cellulose and paper works and prepared paper exclusively from cellulose,without rags. In 1871, an English and Swedish Company started five large works in Sweden. In 1876 Germany had six mills using the caustic soda process.

Jullion obtained a patent in 1855 for the manufacture of pulp from wood by the action of alkali salts (Cross and Bevan: "Wood Pulp and its Uses") . Chauchard obtained an English patent in 1856 for the manufacture of paper and pasteboard from wood or other vegetable substances by treating with an alkaline wash.

In 1856 Houghton, (J.Soc.Chem.Ind. 5, 273.) as a workman in a paper factory, had occasion to use a wooden plug in a vat used for treating esparto. He noticed, after the cooking, that the plug was partly disintegrated and subsequently found that with stronger alkalies and steam pressure the wood disintegrated. The following year he patented the process.

J. Watt obtained a patent in 1861 (Eng.Pat.1507; Chem.News 5,335.) for treating fibrous substances with sodium and potassium carbonates at boiling temperature until the fibers are loosened and separated.

Mathieson(Dingl.Polyt.J. 251, 411.) ~~xxxxxx~~ in 1861, heated wood with alkalies under pressure.

M.Mene (Chem.News 22, 192.)allowed shavings to stand in water for a time, thus removing many substances; then washed with boiling water, steamed, and treated with alkali.

Sinclair (Dingl.Polyt.J.204, 341.) treated wood with strong lye under pressure of about fourteen atmospheres, while Ungerer (Ibid.) required only five to six atmospheres pressure, half the quantity of soda, and one-fifth the amount of chloride of lime for bleaching.

A.Ungerer(Dingl.Polyt.J. 219,367.) makes the solution pass through the wood from one digester to another, and recovers the soda by evaporating the liquor.

V. E. Keegan (Dingl.Polyt.J.208, 316.) digests wood in an iron cylinder with caustic soda solution of 20° Baume,under pressure of 50 pounds to the square inch for a half hour, and then heats the wood by steam to about 300° F.

M.Faudel (Dingl.Polyt.J.219, 428-436.) treated wood with caustic soda solution of eight to ten degrees Baume, under pressure of ten to fourteen atmospheres, obtaining a pulp extremely well adapted for paper making. The drawbacks to the process were : 1st, the loss of the soda, --- the brown liquor from the wood was boiled down and strongly heated--- 2nd, consumption of fuel; 3rd, the destruction of the iron vessels.

J.Ubertin obtained a patent (D.R.P. Kl.55, Nr. 37201, 1886; Dingl. Polyt.J. 262, 284.) for treating straw or wood with a solution of 2.27 parts potassium hydroxide, and 3.37 parts sea salt in 96.16 parts of water, without cooking, in a hollander, having previously crushed the material. In 1886, T. A. Reid, (J.Soc.Chem.Ind. 5, 274.) writing on "Wood as a Paper-making Material", gave the following method used at that time: the wood, barked, was cut into chips, put in a

digester and nearly covered with 20 per cent. of 70 per cent. caustic soda solution. The steam was then turned on and the pressure raised to 120 pounds, where it was kept for two to three hours, then shut down and the digesters blown off. From several experiments on various woods, he gives the following results:

Wood	Class	Per cent. of Cellulose or Fiber	Class of Fiber
Beech	Hard	38.5	Short
Birch	"	42.0	"
Hemlock	Soft	37.5	Long
Poplar	"	41.0	Medium
Scotch Fir	"	39.0	Long
Spruce Fir	"	38.0	"

He obtained excellent results heating with dry heat, to 120 pounds pressure, equivalent to a temperature of 340° F., for two hours with the above solution.

E. Misch (Eng.Pat.16408, 1890; J.Soc.Chem.Ind. 10, 1022.) steamed the wood for three to four hours to remove resinous materials, thereby preventing the acidification of the soda lye, and making it possible to reuse the lye until viscous. He used a soda lye solution of 1.0069 to 1.598 Sp.G. and heated under pressure of five to six atmospheres.

Ch.Arendt and G. de la Rayere (Nr.154754, Kl.55,b, 1902; Zeit. angew. Chem. 18, 1989.) treated wood with a warm solution of an alkali or alkaline earth base, and then, with an alkali carbonate solution.

P.A. Sparre (Eng.Pat. 29118, 1909; J.Soc.Chem.Ind., 30,80.) made paper from sawdust by treating it in an open vessel with five to ten per cent. alkali or acid solution, at a temperature not to exceed 80° until it has lost half its weight. This product was then subjected to the usual operations of digesting under pressure.

F. J. Schreyer (Fr.Pat. 431044, 1911, under Int. Conv. 1910.) made pulp from waste wood by treating it in perforated cylinders placed inside boilers, at 15 atmospheres pressure for about an hour, with two to four per cent caustic soda solution, and then disintegrating on screens by powerful jets of very dilute caustic soda solution or water.

These patents have all had their effect upon the caustic alkali process, so that the process now, as outlined above, is entirely different from that used by Watt and Burgess, having been improved from time to time.

Caustic Alkali Waste Liquors.-- Nearly all the work carried out upon the waste liquors from the alkali cellulose process has been upon the recovery of the caustic soda, but little having been done to recover or utilize the organic material contained in them.

M. L. Griffin(J.Am. Chem.Soc. 24, 235.) analyzed the spent liquor from the soda cellulose process, having a specific gravity of 1.08 (or 10.66° B.) at 15°, and found it contained 14 to 15% deliquescent material, when dried, at 100°. The dried solids gave the following analysis:

	Per cent.
SiO_2	0.11
Fe_2O_3, Al_2O_3	0.02
CaO	0.05
MgO	0.00
K_2O	0.69
Na_2O	25.65
CO_2	3.43
Absolute Acetic Acid	9.89

	(Per cent.)
Organic material extracted,	
by naptha boiling below 60°	1.56
by ether	7.14
by absolute alcohol	28.02
by water	17.02
Total alkalies after incineration	44.25

T. A. Reid,(J.Soc.Chem. Ind. 5, 273.) in speaking of the recovery of soda from the spent alkali liquor, stated that only the liquor blown off could be profitably worked. Its specific gravity is 18-20° Tw. It represents 90 per cent. of the original soda, and contains 80 per cent. water together with matters extracted from the wood, organic and mineral. The solution is evaporated and calcined, obtaining crude sodium carbonate, containing 50-53 per cent Na_2O, a little free carbon, and sodium sulphate and sulphide. This ash is dissolved in water to 20° Tw. and causticized with lime, thereby recovering 80 per cent. of the soda. It is more profitable to distill the dry waste at a low temperature and obtain acetic acid, methyl alcohol and other substances.

F.Müllner(Papier Zeit. 23, 19, 678.) obtained an Austrian patent for the recovery of by-products from the waste liquors of the soda process, by adding bauxite and aluminium salts, and injecting carbon dioxide, thereby precipitating the aluminium as the hydroxide. The alkali remains in the solution and may be recausticized, The aluminium hydroxide may be used for making aluminium salts, or treated with sulphuric acid and used for sizing paper.

Researches by R. Irvine(J.Soc.Chem.Ind. 18, 1097.) showed that it was economically possible to evaporate the liquor and causticize with lime. E. Misch (Eng.Pat. 16408, 1890.) reused the soda lye

until it was viscous, evaporated and subjected to fractional distillation. He obtained valuable neutral hydrocarbons. The residue was ignited and the soda recovered by causticizing.

Bergström and Fagerlind (Järnkontorets Ann. 1908, 575, 679; Chem.Zeit. 32, Rep., 513.)condensed the products coming from the "blowing off" in the manufacture of cellulose by the caustic soda process, and subjected the mixture to fractional distillation. They found the following in the distillates: hydrogen sulphide, methyl mercaptan, methyl sulphide, ammonium sesquicarbonate, acetone, methyl alcohol, and crude turpentine, the two latter in sufficient quantities to be profitably recovered.

I.Kitsee(U.S.Pat.942207,1909.) recovered the caustic and resinous matter of the spent liquors by electrolysis of the solution placed in the anode compartment, while a salt solution is placed in the cathode compartment.

E.L. Rinman (Ger.Pat.222302,1909; 213254, 1910; U.S. Pat.1,005,882, 1911.) precipitated ulmous material from the waste liquor by treating with carbon dioxide in the presence of salt, at a temperature of 75° C. This material was distilled to form acetone, methyl alcohol, etc.

From the resolution of one kilo of pine wood with caustic soda Rinman (Papierfabr. 10, 39-41, 101-104.) obtained approximately the following products and yields: oil of turpentine, 4.0 grams; wood spirit 5.0; ammonia and amines ?; resins, resin oils, and fatty oils, 7.5; carbon dioxide ?; humus and humic acids, 310; humic acids soluble in water, lactones and lactonic acids, 200; acetic acid, 30; formic acid, 30; cellulose, 370 grams.

A patent has been granted Rinman (U.S.Pat. 1,017,320, 2/13/12.) for the precipitation of the soda as sodium bicarbonate, by first removing the organic substances capable of being precipitated by carbon dioxide, and then saturating the liquor with carbon dioxide at a suitable concentration and temperature.

J.M. Neil (Fr.Pat. 442850, 4/23/12.)precipitated the organic matters from the black lyes by first adding an alkali compound in which "a metal acts as an acid radical" , preferably sodium aluminate or sodium zincate, and then heating and agitating with the addition of sodium bicarbonate or the passage of carbon dioxide through the liquid. This treatment precipitates both the metallic compound and the organic matters, leaving a clear lye upon filtration which may be recausticized by treatment with lime. Resins and similar compounds may be obtained from the precipitate by extraction and the metallic oxide recovered by incineration of the residue.

Although fully 50 per cent. of the original wood is dissolved in the black liquors of the caustic soda process, very little is done to recover or utilize this material. The present method of treating the liquors is for the recovery of the soda only. This is accomplished by evaporation to pasty consistency, and then feeding this material into the upper end of a slanting rotary furnace, where the water is driven off, the organic matters burned, and the sodium salts converted largely into the carbonate. This crude soda ash, which comes from the lower end of the furnace, is treated with water, and causticized with milk of lime.

The caustic alkali process yields a high grade of pulp at a minimum expense, since the solutions do not corrode the digesters or furnaces, and at least 90 per cent. of the soda can be recovered. It has none of the objectionable features of the sulphite, the sulphide or the sulphate processes, and is applicable to all fibrous materials. If marketable products could be obtained from the black liquors, the process would very soon displace the sulphite process, and become the most important.

Treatment of Resinous Woods.- During the past decade there has been a strong agitation against the present wasteful method of obtaining turpentine and resins, since the supply bids fair to be exhauseted in a short time unless greater economy is exercised or a new source of material is found. A great deal of resinous wood is used in the paper industry, the resins being dissolved out by the digestion liquor and going to waste. If these could be removed before digesting, the yearly output would be greatly increased. Several patents have been granted for different methods of obtaining the terpenes and resins from this source, but their application has been limited.

W. Hoskins (U.S.Pat. 770463,1904.)obtained a patent for subjecting resinous wood to the action of steam below the temperature which would cause the decomposition of the resins. Volatile condensable constituents are separated from the wood and the resins melted out. The fibrous wood remaining was treated with caustic

soda or other substances to reduce it to pulp.

Craighill and Kerr(U.S.Pat. 817960, 1906; J.Soc.Chem.Ind. 25,494.) chemically treated wood at a moderate temperature to fix the volatile acids and oils and expel the terpene. This solution contained resinous substances, acids, etc. It was withdrawn and worked up. The wood remaining was treated first with caustic soda and then with sodium carbonate solution.

As a result of work done in this laboratory, G. B. Frankforter was granted patents (Canadian Patents 102226-7, 1906; U.S.Patents 918989-90, 1909.) for the extraction of turpentine and resinous materials from wood. Low boiling organic solvents were used. They were condensed directly upon the finely divided wood, thereby obtaining the greatest penetration. The solvent, containing the extracted material, was made to flow back into the boilers where it was reused. After all the resinous material was extracted, the last traces of the solvent were removed by allowing water or caustic soda solution, at a temperature above the boiling pointof the solvent, to flow in at the bottom of the tank thereby volatilizing the solvent. By repeated use of the solvent it became saturated, and deposited the resinous material which was drawn off from time to time. The wood was finally converted to pulp. The whole process was carried out in one apparatus.

W. J. Hough was granted a patent (U.S.Pat.903859, 1908) for treating wood with dry steam to remove the terpene. The moisture was expelled and the wood finally converted to pulp, the entire process being carried on in one apparatus.

F. A. Saylor obtained a patent(U.S.Pat.1,004,473, 1911.) for making paper pulp from resinous wood. The turpentine and resins were extracted by subjecting the wood, mixed with a small per cent. of dry caustic soda, in a closed vessel, to the action of steam at a low pressure, a vacuum being created. The vessel, both inside and out, was subjected to the action of steam at 80-100 pounds for about an hour. On opening a valve at the top the turpentine escaped and was condensed, while the resin was tapped off at the bottom. The pressure of the steam was maintained and the wood submerged in a 15° Baume caustic soda solution. The pressure was then raised to 120 pounds, and after a short time the turpentine and resin were again allowed to escape. The wood was finally digested for five to six hours at 120 pounds pressure.

These processes partially solve the problem, but as yet this field is only slightly developed.

A complete bibliography of the sulphite, the sulphide, the sulphate, and the caustic alkali cellulose processes, has been given above, even though experimental work has not been carried out upon all of them. This has been done because the literature on these processes has never before been brought together in this way, and because such a bibliography should be of great value to anyone wishing to carry on research along any of these lines.

Experimental Part.

The original work, which led to the study of the alkali waste liquors, and to the study of the resin of the Douglas Fir, was begun with the idea of finding some economical method for the utilization of the immense wastes in the lumber industries of the West. As has already been indicated, there are immense quantities of waste in the lumbering and working of the Douglas fir. If this material could be utilized, the greatest waste wood problem in the West would be solved.

In order to determine the effect of treating this variety of wood under different conditions with salt and alkalies, a series of experiments was carried out, first, by using salts alone, then salts and alkalies together, and finally alkalies alone. Solutions of the following were used: sea salt(or concentrated sea water), sodium chloride, magnesium sulphate, lime water and milk of lime, sodium chloride and hypochlorite, bleaching powder, sodium acid sulphate, and mixtures of these with caustic soda. In every experiment the wood was attacked to some extent, and the solutions darkened, but unsatisfactory results were obtained except where caustic alkalies were used. This is, of course, the basis of a well-known commercial process for the manufacture of wood pulp.

As the wood was not sufficiently disintegrated for paper pulp in any case except where caustic alkalies were present, it was evident that none of these treatments would be profitable unless something of

commercial value could be obtained from the solutions in addition to converting the remaining wood into pulp: to determine the nature of these solutions a brief study of them was undertaken .

The solutions which did not originally contain alkalies gave an acid reaction, but some were more strongly acid than others. The solution obtained from the treatment of the wood with a magnesium sulphate solution reacted most strongly acid. This solution was obtained by digesting 350 grams of wood with 1850 c.c. of a 11° Baume solution of magnesium sulphate, under pressure, at 150° for three hours. This yielded 1225 c.c. of the liquor after filtering. Four hundred cubic centimeters of this solution were distilled, first, on a water bath until ten c.c. had passed over, and then with an open flame until 200 c.c. of distillate had been collected. All the distillate came over between 99°and 99.5°. The first ten c.c., as well as all the main portion of the distillate was strongly acid. The last of the distillate which came over was also strongly acid, as was the residue in the flask. Two titrations of 10 ccc. portions of the main distillate with deci-normal sodium hydroxide, required 6.1 c.c. and 6.2 c.c. respectively to neutralize. The solution had a strong reducing action when treated with Fehling's reagent. It being a possibility that the wood might have reduced the magnesium sulphate, thereby forming a sulphite in solution, the distillate was tested for sulphur dioxide, but none was found. Under the circumstances the acid must have been organic, which would limit it to formic acid, or one of the volatile phenols. Since it showed such strong reducing properties, it must have been formic acid. If we

consider it to be formic acid alone, we will have present in the 200 c.c of the distillate 5.64 grams of the acid. The solution remaining in the flask required 43 c.c. of 10 per cent. sodium hydroxide and 350 c.c. of .047828 normal calcium hydroxide to neutralize it. Considering formic acid alone to be present in the solution, the 400 c.c. would have contained 10.585 grams of the acid, or 32.417 grams in the 1225 c.c. Therefore this treatment of the wood yields nearly ten per cent. acids, mostly formic acid.

To determine the source of this acid, whether from the resins or the wood, which had been extracted from the wood, and also wood from which the resinous material had been extracted, were treated separately with magnesium sulphate solution under the above conditions. The solution from the treatment of the resin gave no acid reaction and did not reduce Fehling's reagent, while the solution from the treatment of the wood reacted acid, and did reduce Fehling's reagent. Consequently the acid must have been caused by the ~~action of the~~ action of the sulphate upon the ligno-cellulose. At the temperature and pressure used, the magnesium sulphate is hydrolyzed and forms an acid which breaks up the lignone to some extent, yielding formic acid.

The liquor obtained from the treatment of the wood with the sea salt solution was also acid. It, as well as the distillate from a portion of it, showed a strong reducing action on both Fehling's reagent and ammoniacal silver nitrate.

Both the magnesium sulphate and the sea salt liquors were extracted with ether and the ether allowed to evaporate spontaneously.

In both cases a thick, viscous, dark-red residue was obtained. It reacted acid, had a bitter taste, and had a very strong reducing action on Fehling's reagent. The odor of the mass was that of eugenol.

A portion of the magnesium sulphate liquor was neutralized with milk of lime, the precipitate which was formed was filtered off, and the excess of calcium precipitated with carbon dioxide. To this clarified solution yeast was added, and the solution set aside to ferment. After allowing to stand for four days, a part of the solution was distilled. The distillate was tested for alcohol by the iodoform test. A slight test was obtained. On allowing the remainder of the solution to stand for two weeks at room temperature, a light bluish-green fungi appeared on the solution, entirely covering it in three days. The distillate from this solution gave a stronger test for alcohol. The liquor obtained by digesting wood in a ten degree Baume solution of sea salts, when treated in a similar way gave a slight test for alcohol. Further experiments were carried out upon these liquors, but the results were very unsatisfactory, the distillates giving only faint tests, and in some cases no test, for alcohol. While the first experiments gave encouraging results, the later ones seemed to indicate that the iodoform came from other substances, or that the conditions in the earlier experiments were more favorable. The liquors had a sugary odor, but further work will be necessary to establish the presence of fermentable sugars.

To determine what sugar was present in the solution, a portion of the magnesium sulphate liquor was evaporated to dryness, dried at 100° for two hours and then extracted with absolute alcohol. The residue left after evaporating the alcoholic solution to dryness was then extracted with a small amount of water. This solution was treated with phenylhydrazine in glacial acetic acid and heated in a water bath for twenty minutes. A crystalline substance was obtained. On recrystallizing from alcohol, it melted at 156°, However, after several recrystallizations, the melting point was 189°--190°. This indicates that galactose was present in the solution as its osazone melts at 196°.

The action of all the salts and mixtures of salts on wood, as mentioned above, was briefly studied, but no data of importance was obtained; consequently this work was discontinued and experiments were begun upon the black liquors from the caustic soda process. Since considerable work has been done in this laboratory upon the treatment of Douglas fir wood with various strengths of caustic soda, only slight attention was given to the quality of the pulp, making digestions which, according to previous experiments, had given best results. Unpublished results obtained in this laboratory by Sheldon H. Smith are summarized in the following table: --

TABULATED REPORT OF DIGESTIONS.

No.	Douglas Fir wt.100 gms.	Apparatus	Press.in pounds per sq.in.	Time of Digestion hours	Liquor used	Character of Pulp: Color	Character	Fiber
1	Shavings Ether Extracted.	V.F.L.pump digester	54	3.0	700 c.c. 10%NaOH	very dk, brown	hard	Not completely broken down.
2	"	"	50	6.0	500 c.c. 10%NaOH	light brown	fair	Partially broken down
3	"	"	75	2.0	"	"	"	"
4	Sawdust Ether Extracted	V.F.L.#1302 automatic gas shut off	100	1.0	" 250 c.c. H_2O	very light color	good	Well broken down, but short.
5	"	"	50	1.0	"	dark	poor	Poor, short.
6	"	"	70	1.0	"	medium	fair	Fair,but short
7	"	"	85	1.0	"	better i.e. lighter	Still a little coarse	Not long enough.
8	"	"	100	1.0	"	good	fair	Still short
9	"	"	100	2.0	"	good	good	Short
10	Sawdust and a few large pieces,Ether Extracted.	"	100	1.5	500 c.c. 10%NaOh 75 grams NaCl	good	good	Good. The larger * pieces were also longer and better fiber.
11	Large Chips unextracted	"	100	2.0	"	light	good	Good long fibers.*
12	" extracted	"	100	3.0	"	very"	good	Long and silky. *
13	200 grams unextracted	"	100	2.0	400 c.c. 10%NaOH 15%NaCl	light	good	Fair. *

* This pulp was later decolorized with bleaching powder.

R. P. McMiller and H. A. Halvorson, working in this laboratory, (unpublished work on Wood Cellulose) treated wood with caustic soda solution containing copper sulphate. They digested 200 grams of wood in 900 c.c. of ten per cent. sodium hydroxide solution containing 27 grams copper sulphate, for four hours at a temperature of 180°, and at a pressure of 10 kilograms. A very finely divided product was obtained which was dark-colored and bleached with difficulty. The fiber seemed to be completely destroyed, the product being remarkable in that it could be pulverized. It had the peculiar property of reducing Fehling's reagent. It was insoluble in all the ordinary organic solvents, but soluble in zinc chloride solution. A product having similar physical properties was obtained by digesting wood in a ten per cent. sodium hydroxide solution, containing 5 per cent. sodium chloride, the time of digestion and the pressure being the same, the temperature being 155°. This product bleached easily and did not reduce Fehling's reagent.

To obtain the liquor for this work, wood shavings were digested with a solution containing 5 per cent. Na_2O, having a specific gravity of 10° Baume, for three and a half hours, at 175° and nine to ten kilograms pressure.

Oil.- On opening the digesters while still warm (70°) a pleasing odor was noticed, and a small amount of an oily substance was found on the top of the digesters. The odor was the same as that given off from digesters in factories making oxalic acid from wood. It was found possible to extract this oil from the liquor by ether. Later, however, it was obtained more easily, and in a purer form by steam

distillation. The oil collected on the top of the distillate and was removed by extracting with ether, about two cubic centimeters being obtained from three liters of the black liquor.

When about 50 c.c. of the oily substance had been obtained, attempts were made to distill it at ordinary pressure. Very little came over below 105°. As soon as the temperature was raised above thos point the liquid began to bump and also sputter as though it contained water; consequently further distillation was carried on at a reduced pressure of 20 m.m. A small amount of material came over between 45° and 90°, but the liquid did not begin to boil until a temperature of 90° was reached. From this point the temperature rose rapidly to 105° and then gradually to 110°, where it became constant, remaining at this temperature until nearly all of the substance had distilled over, indicating that most of the liquid was a single substance. The temperature rose gradually from this point to 120° , and rapidly from 120° to 230°, where the distillation was discontinued, a small amount of material still remaining in the flask. Three fractions were collected between 105° and 120°. These were fractionally distilled again at 13 m.m. pressure. A small amount of material distilled over below 98°, but most of it came over at 102° where the temperature remained constant. Three fractions were collected between 98° and 109°. These were fractionally distilled at ordinary pressure. The temperature rose rapidly to 199° and became constant at 200° to

201°, and at 205° only a very little material remained in the flask. A fraction was collected between 199.5° and 202°, and a second between 202° and 205°. Since the largest fraction in each distillation was collected at a constant temperature, this fraction must have been a single chemical substance. That fraction distilling between 199.5° and 202°, with constant temperature at 200° to 201°,was considered to be pure, and was used to determine the properties of the substance.

When first distilled every fraction of each distillation was of a very light straw color, but on standing for a few hours they turned into a deep, brownish-red color. This was probably due to oxidation, for on long standing the liquid became almost black.

This substance was found to be readily soluble in all the ordinary organic solvents, but insoluble in water. When an aqueous solution of ferric chloride was added to a weak alcoholic solution of the substance, the solution became dark green, changing gradually to a deep olive-green, and after ten minutes to a deep, orange-red. The color was destroyed by the addition of hydrochloric acid. This indicated a phenol.

The substance was treated with metallic sodium, with which it reacted readily, even in the cold, indicating that a hydroxyl group was present in the compound.

The molecular weight of the substance was determined by the freezing point method, using benzene as a solvent. The following results were obtained:

Wt.Substance	Wt. Solvent	Lowering T.	Calculated
.1522	17.1614	.3535	122.9
.0806	17.1614	.1878	122.54

The specific gravity determined at 23.2°, using a 5 cc. picnometer, was found to be 1.01558.

Analysis of the substance by combustion was tried, but the results were not at all satisfactory on account of the volatility of the material. Several methods, such as weighing in a small bulb, were tried, but none of them gave satisfactory results. Finally, weighing in a boat which contained pure copper oxide powder was found to give the most concordant results. The following are the results of three analyses using this method:

I. .2514 gms. of the substance gave .6393 gm. CO_2 and .1883 gm. H_2O

II. .1367 " " " " " .3558 " " " .1048 " "

III. .2040 " " " " " .5369 " " " .1621 " "

	Found		
	I.	II.	III.
C =	69.35	70.9	71.78
H =	8.32	8.53	8.82

The physical and chemical properties, the molecular weight and specific gravity of the substance correspond to those of methyl-phenylcarbinol, however, the analyses do not agree with the percentage composition of this substance, being low in carbon and high in hydrogen.

Lignone Complex.- It has been known for some time (J.Chem. Soc. 72, II, 583.) that a precipitate will be obtained from the black liquors of the caustic alkali process if they are acidified. E. L. Rinman (J.Soc.Chem.Ind.,30, 485.) precipitated the humus material from the solution by means of carbonic acid. This latter method was tested. It was found that all the humus material from the caustic soda liquor was not precipitated by carbonic acid, for if the solution was acidified with mineral acid, after carbon dioxide had been passed into the solution until nothing more would precipitate, a copious precipitate of light, brownish-yellow organic material was obtained.

Even mineral acids do not precipitate all the organic material in the solution, If the clear solution obtained by precipitating the humus material, is evaporated to dryness, and this residue extracted with ether, a red solution is obtained. Organic material only remained upon evaporation of this solution. The alcoholic extract of the dry residue from the liquor had the odor of vanillin. The humus material proved of great interest, so work upon it was started, precipitating it by treatment of the liquors at 65° to 70° with mineral acid.

This humus material is largely that complex which is in combination with the cellulose. It is that part of the wood which is acted upon by the solutions used, dissolving it out and leaving the cellulose. On account of its apparent ketone characteristics Cross and Bevan (Chem.News 64, 63) suggested the name "Lignone" for this non-cellulose constituent of the ligno-cellulose, but Lindsay and Tollens(Zeit.angew.Chem.,1892, 154-158.) called it "Lignin".

Lignone has been the subject of considerable research, but still its true nature is not known absolutely. Sachsse, in his "Chemie u. Physiologie d. Farbstoffe, Rohlenhydrate u. Proteinsubstanzen"(Leipzig, 1877.), gives its composition as $C_{18}H_{24}O_{10}$. In comparing cellulose, $C_{18}H_{30}O_{15}$, with this formula for lignone, the latter could be formed from the former by dehydration (minus 3 H_2O) and deoxidation(- O_2). He gave the following hypothetical equations:

$C_{24}H_{40}O_{20} - C_6H_6O_5 - 5\ H_2O = C_{18}H_{24}O_{10}$.

Lindsay and Tollens(Chem.News 64, 63; Zeit.angew.Chemie,1892,154.) working on the waste liquors of the sulphite process, found that 90-95 per cent. of the organic material in solution was an amorphous or gummy material. This was isolated, after preliminary purification, in the following ways, and gave a satisfactory uniformity in empirical composition:

(a) Precipitated by alcohol $C_{24}H_{24}(CH_3)_2SO_{12}$

(b) Gums precipitated by lead compounds (1)$C_{24}H_{24}(CH_3)_2SO_{12}$
(2)$C_{24}H_{24}(CH_3)_2SO_{12}\cdot 1\text{-}1/2\ H_2O$

(c) Precipitated by HCl $C_{24}H_{24}(CH_3)_2SO_{10}$

(d) Precipitated by Br $C_{24}H_{22}(CH_3)_2Br_4SO_{11}$

The authors regarded these bodies as derived from the compound $C_{24}H_{24}(CH_3)_2O_{12}$, and state this to be the empirical formula for the lignone constituents of fir wood.

Lindsay and Tollens do not attempt any structural formula for this compound. However, Cross and Bevan state that it has a ketone structure. Their belief is founded on the results obtained by treatment with hydriodic acid, showing the $O\cdot CH_3$ group, and upon

the obtaining of acetic acid by treating the fiber with sulphuric acid, showing CH_3 groups in combination with CO groups. The products of destructive distillation also show the characteristics of these groups.

H. Seidel (Mitt.d.k.k.Tech.Gew.Mus.N.F.7, 1897, 119-225.) obtained, by various methods of salting out and precipitating, a compound analyzing to a substance having the empirical formula $C_{26}H_{30}SO_{12}$, thus corroborating the work of Lindsay and Tollens.

Klason, writing on the theory of the sulphite cellulose process, (Svensk kemisk tidskrift, 1897, 9, No. 6.) gives the results of his researches respecting the constitution of lignin as showing that: first, lignin is a glucoside, one of the constituents of which is an aromatic compound,- lignyl glycide -- containing two nuclei; second, lignyl glycide contains 18 to 20 carbon atoms in the molecule, and includes the following atomic groups, -- methoxyl, hydroxyl, the glycide residue C_3H_5O and active carbonyl, CO $\overset{C}{H(C-)}$. Lignin is decomposed by calcium bisulphite, with formation of sugar, and the calcium salts of dibasic lignyl-sulphonic acid. Coniferin is similarly decomposed by calcium bisulphite yielding coniferyl-sulphonic acid. He therefore concludes that coniferin contains a coniferyl glycide.

He claims further that if, on account of defective circulation in the cellulose boilers, sufficient lime be not present to neutralize the lignyl-sulphonic acid, the glycide polymerizes to dark-brown resin, insoluble in sulphurous acid. This probably causes the dark-colored pulp obtained in some boilings.

Cross and Bevan, in their recent book on "Wood Pulp and its Uses", state again that the parent molecule or lignone complex of the wood may be considered as having the composition $C_{24}H_{24}(CH_3)_2O_{10}$.

G.Guerin(Compt. rend. 1897, 125, 311-12; J.ChemSoc . 73, II.583.) macerated wood for two or three days with a one per cent. solution of caustic potash, obtaining a deep brown liquor, which yielded a bulky, flocculent precipitate when acidified with hydrochloric acid. This precipitate was washed with weak hydrochloric acid solution, redissolved in ammonium hydroxide, reprecipitated by acid, washed and dried. By subjecting beech wood to this treatment, a pale brown powder was obtained having the following percentage composition: C = 56.792, H = 5.04, N = 4.60, S = 0.660, P = 1.297, Mn = 0.402.

H. Seidel (Zeit.angew.Chem. 1900, 951-956.) states that the mother substance of lignone-sulphonic acid, is lignone. When calculated free from SO_2, it contains C, 64 per cent., H, 6 per cent. and O, 30 per cent.

In discussing the functions of the caustic soda process (J.Soc. Chem. Ind. 26, 561.) J. A. DeCew states that the chemical reactions of the process consist in the combination between the alkali radical and the more reactive portions of the wood, which, under the influence of temperature and pressure breaks down with the formation of soluble products, and leaves cellulose in the form of isolated fibers. The action is one of hydrolysis in which the woody molecule is gradually broken down with the formation of acid products which combine with and neutralize the alkali. At first the reaction is rapid but it soon becomes slower. It is a general principle applying to

any woods, that the resistance to hydrolysis increases with the lignification, the latter depending upon the age of the tree and the rate of growth.

If the wood did not contain resins, terpenes or other similar substances, being nothing but pure ligno-cellulose, the humus material precipitated by neutralizing with hydrochloric acid the liquor obtained by digesting the wood with caustic soda solution, should be lignone. Analysis of this precipitate would give the composition of the lignone complex.

To test this supposition, 400 grams of wood was extracted with benzene in large soxhlet tubes, for two days. Only a very small amount of resin was obtained, as was expected since the wood had been drying for several years, and had been in the form of shavings for over a year. The wood was then freed of benzene and digested for three and a half hours in 4500 c.c. of 10° Baume sodium hydroxide solution, at 175° and 10 kilos pressure. From this digestion 3600 c.c. of 11° Baume black liquor, and 175 grams of air-dried pulp was obtained. Some of this liquor was neutralized with hydrochloric acid at 60° to 70°, the precipitate filtered off, washed free from chlorides, dried at 100° for two hours, and analyzed.

The following are the results of two analyses of this precipitate:

I. .2584 gm. of the dry material gave .6142 gm. CO_2 and .1211 gm. H_2O

II. .2420 " " " " " " .5690 " " " .1130 " "

Calculated for $C_{24}H_{20}(CH_3)_2O_9$	Found I.	Found II.
C = 64.73	64.82	64.12
H = 5.37	5.206	5.188

These analyses indicate that the lignone constituent of Douglas Fir wood is not the same as the lignone of Lindsay and Tollens. They considered it to be a compound $C_{24}H_{24}(CH_3)_2O_{12}$, while Cross and Bevan considered the parent substance to be $C_{24}H_{24}(CH_3)_2O_{10}$. If either is the parent molecule, then the lignone of Douglas Fir would be a dehydration and reduction or oxidation product represented respectively by the following equations:

$2C_{24}H_{24}(CH_3)_2O_{12} -- 4H_2O -- O_2 = 2C_{24}H_{20}(CH_3)_2O_9$ or

$C_{24}H_{24}(CH_3)_2O_{10} -- H_2O -- H_2 = C_{24}H_{20}(CH_3)_2O_9$

Analyses of the precipitate obtained in the same manner by digesting unextracted wood, gave the following results:

I. .2924 gm.of the dry material gave .6965 gm.CO_2 and.1503 gm. H_2O

II. .3597 " " " " " " .8515 " " " .1747 " "

III. .3456 " " " " " " .8215 " " " .1712 " "

	Found		
	I.	II.	III.
C	64.95	64.57	64.82
H	5.71	5.39	5.50

These results are very similar to those obtained above, corroborating them, and also showing that the resin content of the wood was very small.

This humus material was found to be entirely soluble in acetone and ammonium hydroxide, but only partially soluble in ether, alcohol and benzene. The ether extract was entirely soluble in alcohol but the alcohol extract was only partially soluble in ether. This would

indicate that the material was not a single chemical substance but a mixture.

In order to separate this humus material into its constituents, and consequently determine more definitely the nature of the lignone, the material precipitated by hydrochloric acid from the liquors obtained by digesting unextracted wood, as already described, was extracted with ether. A very dark-red, extremely viscous mass was obtained. It had an acid reaction, gave the ferric chloric test for phenols, and was entirely soluble in alcohol, acetone, benzene, glacial acetic acid and ammonium hydroxide. No analysis of this extract was made, since it did not appear to be a single chemical substance but a mixture of several. After several attempts to resolve it into its constituents, fractional distillation at a pressure of 15 to 20 m.m. was found to give the best results. Fractions were collected up to 285°, redistilling and fractionating several times. Nearly every fraction in alcoholic solution gave the ferric chloride test for phenols; many of them reduced Fehling's reagent.

On allowing the distillate, which came over between 190° and 200° at 15 m.m., to stand, a crystalline acid separated out. On recrystallization from ether triclinic prisms, melting at 111.5° -112°, were obtained. They were soluble in warm water from which they recrystallized on evaporating spontaneously. They were soluble in cold dilute ammonium hydroxide, depositing needle like crystals upon evaporation. The crystals were identified as pyro-tartaric acid.

The residue of the humus material, insoluble in ether, was analyzed and gave the following results:

I. .3336 gm. of the dry material gave .7675 gm. CO_2 and .1670 gm. H_2O
II. .39085 " " " " " " .9089 " " " .1875 " "
III. .2761 " " " " " " .6380 " " " .1353 " "
IV. .3182 " " " " " " .7405 " " " .1549 " "

Calculated for	Found			
$C_{24}H_{20}(CH_3)_2O_{10}$	I.	II.	III.	IV.
C = 62.65	62.73	63.40	63.03	63.47
H = 5.22	5.56	5.33	5.46	5.41

After extracting the humus material with ether, the residue was extracted with 95 per cent. alcohol. Upon the addition of either water or ether to this solution, a copiuos precipitate was obtained which, upon drying at 100° for two hours gave a very drak brown powder.

The following are the results of two analyses upon the material precipitated from the alcoholic solution with ether:

I. .2722 gm.of the dry material gave .6266 gm. CO_2 and .1325 gm. H_2O
II. .2372 " " " " " " .5381 " " " .1116 " "

Calculated for	Found	
$C_{24}H_{20}(CH_3)_2O_{10}$	I.	II.
C = 62.65	62.77	61.87
H = 5.22	5.41	5.23

Three analyses of the material precipitated from the alcoholic solution with water, gave the following results:

I. .2844 gm. of the dry material gave .6444 gm. CO_2 and .1374 gm. H_2O
II. .3738 " " " " " " .8289 " " " .1781 " H"
III. .3205 " " " " " " .7193 " " " .1539 " "

	Found		
	I.	II.	III.
C	61.80	60.47	61.20
H	5.37	5.29	5.21

These analyses show that this material is very similar to that precipitated by ether. Although a lower percentage of carbon was found to be present in the substance precipitated by water, it may be considered to be the same as that precipitated by ether. If this is considered to be a derivative of the parent lignone, it would be a dehydration product of the parent molecule of Lindsay and Tollens and an oxidation product of the molecule of Cross and Bevan. We might represent these respectively by the following equations:

$C_{24}H_{24}(CH_3)_2O_{12} - 2H_2O = C_{24}H_{20}(CH_3)_2O_{10}$ or

$C_{24}H_{24}(CH_3)_2O_{10} - 2H_2 = C_{24}H_{20}(CH_3)_2O_{10}$.

The results obtained thus far indicate that the lignone of the Douglas Fir is not the same as that found in other woods by either Lindsay and Tollens or Cross and Bevan. As it exists in the liquors obtained by digesting wood with caustic soda solution, it is not a definite chemical substance, but a homogeneous mixture of several substances, largely phenols. It may exist in the wood as a single substance in combination with the cellulose, but may be broken down into simpler substances by the severe treatment to

which it is subjected in the process of hydrolysis. As such a chemical substance, it would have an empirical formula respresented by the composition of the aggregate precipitated from solution by neutralization. Using the grouping of Cross and Bevan, it would have the composition represented by the empirical formulaa $C_{24}H_2O(CH_3)_2O_9$, and therefore be a dehydration and oxidation product of the parent molecule as given by these men.

The Resins.

The resins are among the most important substances in the phytochemical world, but they are also among the most complex, and are still classed as substances of unknown constitution. Notwithstanding the fact that less is known concerning the chemical nature of the resins than perhaps of any other group of organic compounds, they are doubtless the oldest organic compounds known to man. They played an important part in the chemical industries in the early history of mankind. They were used in almost every phase of early human life, as lacs, varnishes, balsams, perfumes, pomades, and in the art of embalming. They were described by the early alchemists as substances insoluble in water, generally soluble in alcohol, and for the most part noncrystallizable. They are the result of secretive plant fluids, exuding from the plants and hardening in the air. They could not be separated into their constituents by any means known to the early chemists, and were therefore regarded as single substances. As a rule, however, they are mixtures of two or more complex substances, a gum and some volatile oil or terpene. They are known as gum resins or natural balsams, and with the terpenes as oleoresins. As a result of their noncrystalline nature they were generally excluded from the list of substances worthy of investigation.

The earliest investigations on record upon the resins were carried out upon amber by Georg Agricola, in 1546, (Basiliae 1558, 1, IV.). He subjected amber to dry distillation, obtaining a fine white substance which he recognized as succinic acid. This work led to further research, not only upon the resins but upon a great many substances in the phytochemical field. Benzol, toluol, guavacol, and resorcin were among the substances discovered in this period. Benzol was obtained by the dry distillation of benzoic gum, toluol in the same way from tolu balsam, guavacol from guava resins and resorcin from the orcin of resin galbanum.

Nearly all the work upon the resins up to the very last of the eighteenth and the beginning of the nineteenth century, was upon the products obtained from dry distillation. It was not until this time that crystalline compounds were obtained directly from the resins by simple extraction.

Hermbstädt (Berlin Jahrb. der Pharmacie 1795, 105; 1796, 146; 1797, 97; 1791,1.) was one of the first to separate the resins into their constituents. As a result of his researches he stated that the pure resin material is always the same, the other substances present causing the difference in the various resins. A few years later Pelletier (Ann. de chim. 79,90.) determined quantitatively the constituents of opopanax, and John (Chem. Schriften 5, Berlin 1816, 1.) quantitatively resolved gum-lac. Pfaff (System der Materia medica nach chemischen Prinzipien. Leipzig 1814 und 1815, III und IV, Bd.) and Braconnot (Ann.de chem. 68, 19.) should also be mentioned among those who

worked upon the resins during this period. Their work was very important, as they were among the first to undertake the quantitative resolution of the resins.

With the development of the combustion method of organic analysis by Gay-Lussac and Thenard, (Ann. de chem. 74, 1810; Gilbert's Annalen der Physik 37, 1811,401.) previously suggested by Lavoisier, (Mem. de l'acad. 1784.) a new impetus was given to the study of organic compounds. Even in the early development of this method of analysis we find that Gay-Lussac and Thenard made analyses of two resins, the resin of terebenthine and of copal. They found:

	C	H	O
Resin of terebenthine	75.944	10.719	13.337
Copal	76.811	12.583	10.606

As a result of this work the development of organic chemistry in the past century has been phenomenal. Its history is also the history of phytochemistry, and therefore largely the history of the chemistry of the resins. From this period even to the present time, the resins have been the basis of extensive investigation, the most important of which have been carried on by Tschirch and his co-workers.

Until the publication of Tschirch's book, "Die Harz und die Harzbehalter", it had been generally supposed that there was but one resin acid, namely, abietic acid, the differences in the various resins being due to the presence of small quantities of other constituents. This monumental work, however, has established the fact

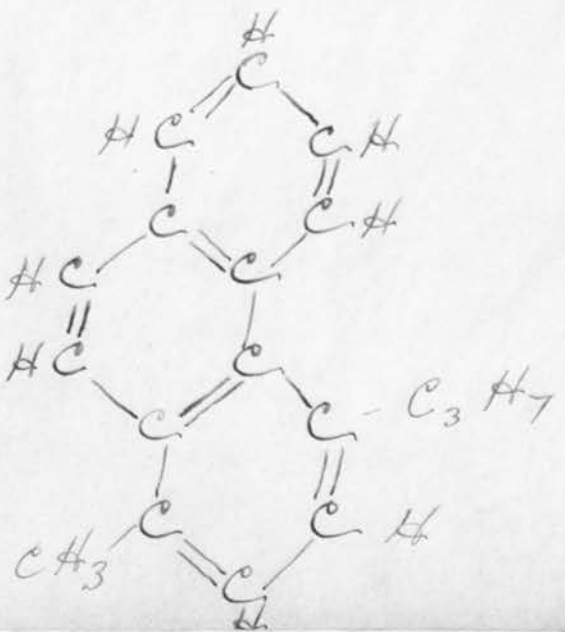
that each resin has its own distinctive acid. There probably is some abietic acid present in most if not in all of the resins, but it is not necessarily the principal or characterizing one. This is also shown by work done in this laboratory on resinic acid (J.Am.Chem.Soc.31, 561.).

Baup (Ann,chim.phys.,31, 108.) did the first work of note upon the resins, obtaining a crystalline substance from Pinus abies, which he named abietic acid, and a second substance from Pinus maritima, which he called pinic acid. Unverdorben (Pogg. Ann. 11-20, 239) obtained two acids from common colophonium, the one amorphous, the other crystalline and similar to abietic acid. He called them pinic and sylvic acids, respectively. Trommsdorff (Ann.13,169.)while working on American colophonium, obtained a crystalline acid which he regarded as sylvic acid, but to which he gave the formula , $C_{40}H_{60}O_4$. Siewert(Z.gesammten Naturwissenschaften 14, 311.)repeated this work and assigned to sylvic acid the formula $C_{20}H_{30}O_2$. He also showed that abietic acid is isomeric with Baup's pinic acid and with pimaric acid described by Laurent(Ann. 34, 372) but differing in physical properties and in its solubility in alcohol.

Maly(J.Prakt. Chem., 96, 145.) obtained an acid which he called abietic acid and to which he assigned the formula $C_{44}H_{44}O_5$. Flückiger (J.Prakt. Chem., 101, 235) gave the formula $C_{20}H_{30}O_2$, to an acid obtained from American colophonium and regarded by him as identical with Maly's abietic acid. Kelbe(Ber. 13, 888.) gave the formula $C_{44}H_{64}O_2$ to a resin oil. Mach(Monatsh. Chem. 13, 627.) claimed that abietic acid

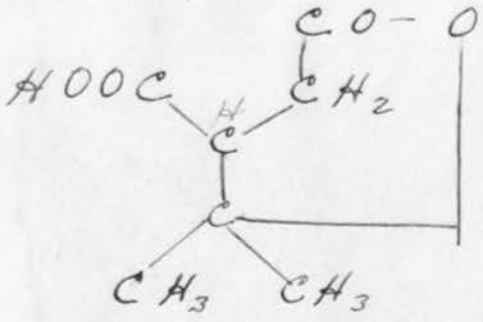
was the only acid in American colophonium and had the formula $C_{19}H_{28}O_2$, differing from pimaric, which has been given the formula $C_{20}H_{30}O_2$. Loos (Diss. Columbia University, 1900) partially corroborated these results. Tschirch and Koritschoner (Arch.Pharm. 240,568,)obtained two acids from Pinus Palustris, palabienic $C_{13}H_{20}O_2$ and palabietic, $C_{20}H_{30}O_2$. These were obtained from what was supposed to be abietic acid. Henry(J.Chem. Soc., 79, 1144.) isolated an acid, $C_{30}H_{45}O_5$,from sandaric resins; he also showed it contained pimaric acid. Tschirch in his work (Die Harz und die Harzbehälter, P. 596) describes Japopinic acid, having the formula $C_{17}H_{26}O_2$, alpha and beta, canadinic acids, $C_{19}H_{30}O_2$ (Ibid.543.), alpha and beta picipimaric acids,$C_{18}H_{28}O_2$(Ibid 605.) and alpha and beta pimaric acids, $C_{18}H_{26}O_2$(Ibid 559.).

It has thus far been impossible to synthesize any of the known resin acids. Consequently it has been necessary to determine their structure from the structure of the products obtained by subjecting them to various treatments. Reten, a hydrocarbon having the empirical composition $C_{18}H_{18}$, has been considered by some to be very closely related to abietic acid. It is the 8 methyl - 5 methylethylphenanthrene(Wahlforss, Zeit.f. Chem. 1869, 73; Ekstrand, Lieb. Ann. 185, 25; Bamberger u,Hooker, ebenda 229, 102.).

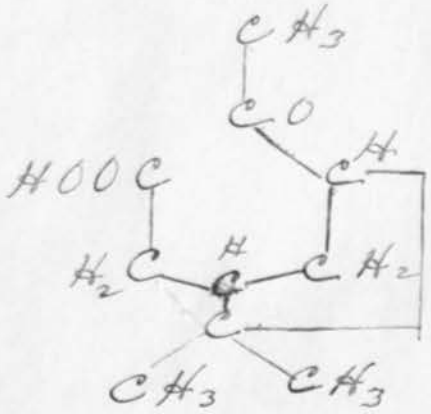


Tschirch (J. de pharm. et de chimie, Nov. 1900; Pharm. Post 1900, No. 43) has published an article on the formulae of abietic acid, based upon the formula of reten, as also upon experimental work.

If abietic acid is distilled with zinc dust in an atmosphere of hydrogen, napthalene and methylnapthalene are obtained along with other substances. Naphthalene is obtained by treating colophonium in the same manner. Terpene is one of the products obtained by distilling colophonium over slaked lime. It also results from heating pimaric acid with hydriodic acid and red phosphorus. Oxidation of abietic or pimaric acid yields terebinic acid (dimethylparakonic acid) which can be obtained from pinene or pinon. Oxidation of abietic acid with alkaline permanganate gives ketonic acid, $C_{10}H_{16}O_3$, the alpha pinonic acid, perhaps the same acid which is obtained in the oxidation of the pinenes with permanganate.

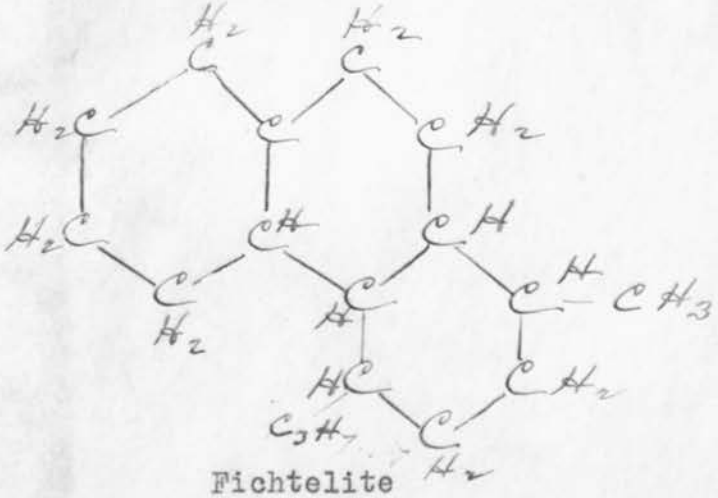


Terebinic acid



alpha Pinonic acid.

These results show that the constitution of the resin acids can be considered to be built up either from the naphthalene or the terpene structure, with the formation of a third ring, as for instance from fichtelite, a hydrocarbon found together with reten on the fossil stems of pinus uliginoso (Hell, Ber.d. chem. Ges. 22, 499; Bromeis, Lieb. Ann. 37, 304; Bamberger, Ber. 22, 635 and 3362; Clark, Lieb. Ann. 103, 237) having the following formula:

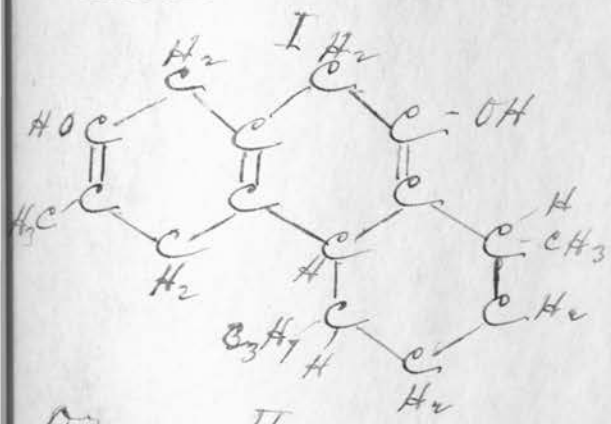


Fichtelite

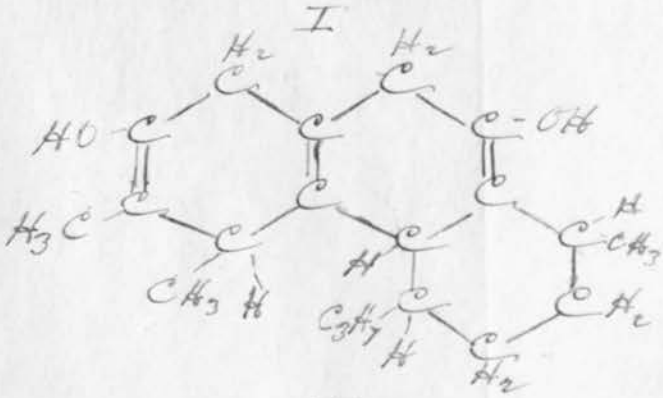
Pimaric and abietic acids may also be derived from the hydrocarbon octohydroreten ($C_{18}H_{26}$) , through which supposition the obtaining of naphthalene of terpene through the influence of heat, seldom obtaining both together, could easily be explained.

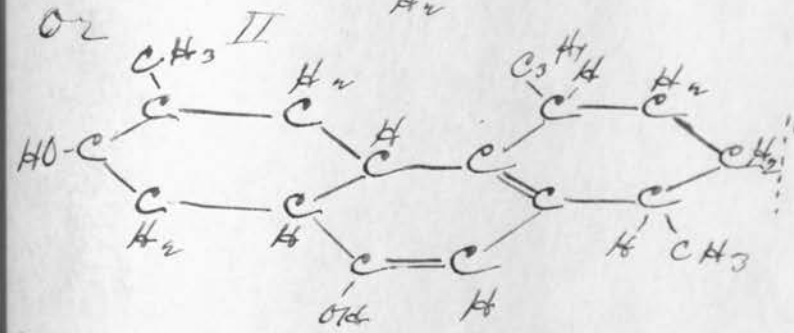
Tschirch proposed the following formulae, the positions of the OH, COOH and CH_3 groups being unknown:

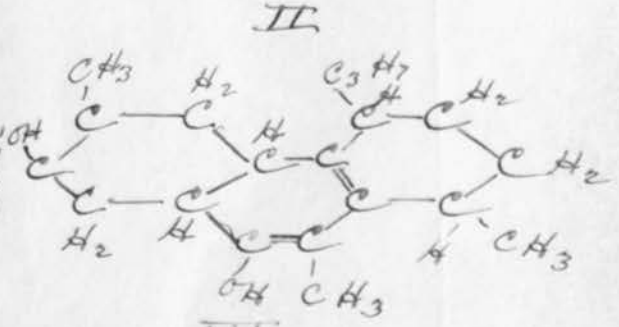
Abietic acid = $C_{19}H_{28}O_2$

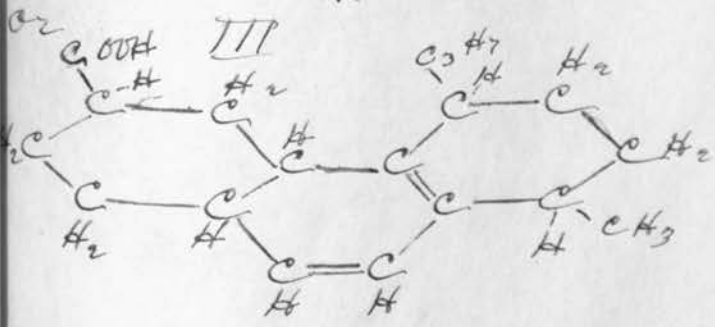


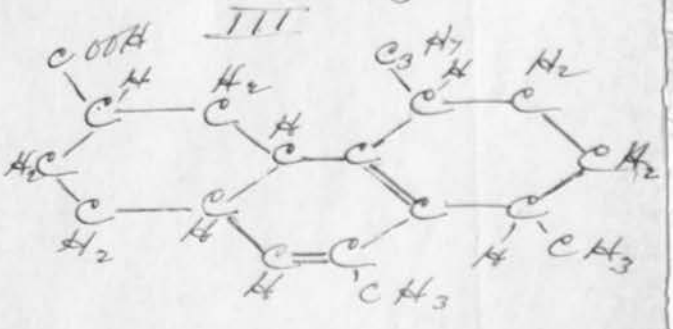
Pimaric acid = $C_{20}H_{30}O_2$











The formulae I and II are based on the supposition that OH groups are present, and formula III on the pressure of the COOH group. He does not state which are present although he is inclined to agree with Endemann (Amer.Chem.J.33, 523.), who claims that abietic acid contains a COOH group.

While the formation of naphthalene, terpenes and other substances can be explained on the basis of the above formulae, there is not sufficient evidence to prove that any one of these formulae represent exactly the composition of the acids. A definite formula cannot be given.

Experimental Part.

The question arose as to whether the substances obtained above in the fractional distillation of the ether extract of the humus material precipitated from the black liquors of the caustic soda cellulose process came from the resins or terpenes or from the wood itself. They did not come from the terpenes since the finely divided wood had been thoroughly dried and only contained a mere trace of the terpenes.

To determine the real source of the above mentioned compounds, 350 grams of resin which had been extracted from the same species of wood were treated with a solution of sodium hydroxide, 250 gms. in 1200 c.c. of water, in an autoclave at 180° for four hours. On opening there was a soft material on the top of the saturated solution, which became hard on standing. It was removed from the liquor, dissolved in hot water and treated with hydrochloric acid until nothing more was thrown down. The precipitate was filtered and washed free from chlorides.

Betic Acid.- $C_{17}H_{24}O_2$.- The material thus obtained differed greatly from the precipitate obtained from the black liquors in the alkali treatment of the wood, and also from the material extracted by ether from this precipitate. It was a light brown, brittle, compact mass. Preliminary tests showed it to be partially soluble in warm 57 per cent. alcohol. On allowing the filtrate to cool it turned milky, and after evaporating spontaneously for a day or two, deposited beautiful white, leaf-like, radiating crystals with saw-tooth edges. These crystals were recrystallized from the same per cent. of alcohol until they had a constant

melting point. Later it was found that 62 per cent. alcohol gave better results, therefore it was used for further extractions and crystallizations.

In order to determine whether this substance occurred as such in the resin itself or whether it was produced by the action of the sodium hydroxide upon the resin, some of the original resin was extracted in the same manner with 62 per cent.alcohol and recrystallized three times. The last crystallization raised the melting point but .5°, indicating that the substance was pure. These crystals were identical with those obtained by the alkali treatment of the resin. They were soluble in methyl and ethyl alcohols, methyl iodide, glacial acetic, ether,chloroform, benzene, ethyl acetate, carbon disulphide, acetone, carbon tetrachloride, pyridine and the alkalies; slightly soluble in 50 per cent. alcohol but insoluble in water and the mineral acids. The melting point of the pure substance was 143.5°-144.5°.

The specific rotation with polychromatic light at 22° was (a)J= -.68

The results of four analyses gave the following:

I. .0990 gm. of dried substance gave .2852 CO_2 and .0834 H_2O
II. .10315 " " " " " .2954 " " .0875 "
III. .1380 " " " " " .3955 " " .1153 "
IV. .1006 " " " " " .2887 " " .0843 "

Calculated for $C_{17}H_{24}O_2$	Found			
	I.	II.	III.	IV.
C = 78.39	78.56	78.102	78.11	78.21
H = 9.296	9.35	9.42	9.28	9.30

The first three analyses were made on the acid which was obtained by direct extraction from the resin and then recrystallized several times after filtering through animal charcoal. The fourth analysis was made on the acid obtained by treating the resin in an autoclave with caustic soda solution.

The following table gives the formulae, the composition (as found by analysis) and the melting points of the resin acids which somewhat resemble betic acid:

Name	Formula	Carbon found	Hydrogen found	Melting point.
Japopinic	$C_{17}H_{26}O_2$	77.73	10.13	153°
Alpha Pimaric acid	$C_{18}H_{26}O_2$	78.73	9.65	90-91°
Beta Pimaric acid	$C_{18}H_{26}O_2$	78.81	9.57	89-96°
Alpha Picipimaric acid	$C_{18}H_{28}O_2$	78.22	10.38	95-96°
Beta Picipimaric acid	$C_{18}H_{28}O_2$	78.56	10.30	93-94°
Abietic "	$C_{19}H_{28}O_2$	78.97	9.84	153-154°
Alpha and Beta Canadinic	$C_{19}H_{30}O_2$	78.55	10.59	95°
Betic acid	$C_{17}H_{24}O_2$	78.25	9.34	143.5-144.5°

It is evident from a comparison of the above analyses and melting points, that betic acid is entirely different from any of the above acids. It also differs from these in its general physical properties.

The molecular weight of the acid was determined by the freezing point method, using benzene as a solvent.

Results were obtained as follows:

Wt. acid	Wt. solvent	Lowering T.	Calculated.
.0850	19.2884	.0491	448.7
.0912	19.2884	.0495	477.6
.1683	19.2884	.091	479.14

As will be seen, the above determinations give results nearly twice as high as those indicated by analyses. This is doubtless due to incomplete polymerization, Beckmann(Zeit.f.Phys.Chem.,2,715.) and Paterno (Gazz. chim. 19, 44.).

The Neutral Equivalent.- Bietic acid gave a sharp acid reaction with phenolthalein in an alcoholic solution. It could, therefore, be accurately titrated with alkalies; even barium hydroxide gave a sharp end point. By this method of titration it was very easy to determine the neutral equivalent of the acid.

The following are the results of four titrations of the acid with .120238 normal barium hydroxide, the acid in each case being dissolved in 50 c.c.of alcohol:

	I.	II.	III.	IV.	V.
Acid in grams	.1686	.1610	.2607	.25015	.2739
$Ba(OH)_2$ in c.c.	4.96	4.78	7.74	7.44	8.2
Neutral equiv.	282.06	280.1	280.2	279.6	278.8

In each determination a correction of 22 c.c. was made as it required that amount of the alkali to exactly neutralize 50 c.c of the alcohol. All the neutral equivalents were calculated by the well-known formula

N.E. = $\frac{1000\ g.}{A \times N}$ where g = gms. of acid, A = numer of c.c. of alkali, and N = the normality of the alkali solution.

After making the first two titrations, the solutions were mixed and distilled water, free from carbon dioxide, was added to precipitate the barium salt. When about 25 c.c. had been added, a precipitate began to form. Before the precipitate appeared, however, the solution became slightly acid. Sufficient alcohol was added to redissolve the salt which had been thrown down, then the solution again titrated. Finally, the salt was precipitated by the addition of water, filtered, dried and a barium determination made.

After the last two titrations, the solution was mixed and the alcohol partially evaporated off before adding water to precipitate the salt. This was done in order to avoid filtering a large amount of solution. As soon as the solution had become warm, the color disappeared. This warm solution was then titrated to red color with the barium hydroxide solution, the color remaining until the solution had been evaporated to a few cubic centimeters and some of the salt had separated out. If the amounts of acids used are added and also the amount of the alkali required to give a permanent color, we shall have obtained the following results:

.52405 gm. acid required 16.6 c.c. barium hydroxide solution of the above indicated strength. This gives a neutral equivalent of 262.5, which is very close to 260, the molecular weight as determined by analysis. This also shows that to obtain the true neutral equivalent of this acid it must be titrated in warm alcohol.

The above results were also verified by titrating with .047824 normal calcium hydroxide solution as indicated by the following determinations:

	Acid	c.c. $Ca(OH)_2$	N.E.
Titrated in cold solution	.1462	11.	278
After warming solution	.1462	11.6	263.6

Three other titrations in warm solutions gave the following results:

Acid	c.c. $Ca(OH)_2$	N.E.
.1058 gm. required	8.5	260.2
.1118 " "	8.7	268.6
.0979 " "	7.7	265.9

The Salts of Betic Acid.- The salts of the acid were prepared and analyzed. However, considerable difficulty was experienced in obtaining the pure salts on account of the weak nature of the acid and the readiness with which they dissociated. Practically all of the salts hydrolyze readily in water, as will be shown later.

Barium Betate,-$(C_{17}H_{23}O_2)_2Ba$. - The barium salt was obtained by precipitating with water from the alcoholic solution as indicated in the determination of the neutral equivalent. The salt was filtered as rapidly as possible, dried for an hour at 105° C. and analyzed.

Analysis gave the following:

.0740 gm. barium salt gave .0254 gm. $BaSO_4$

Calculated for	Found
$(C_{17}H_{23}O_2)_2$ Ba	
Ba = 20.96	Ba = 20.68

On account of the difficulty in obtaining the salt by this treatment, due to the fineness of the precipitate and to hydrolysis, another method was sought. The ammonia salt was prepared by dissolving the acid in dilute ammonia, and then diluting with nearly half the volume of 95 per cent. alcohol. Barium chloride was then added in slight excess, the barium salt being thrown out as a white, curdy precipitate. The salt was filtered off and washed with distilled water free from carbon dioxide. It was impossible to obtain a filtrate which did not give a cloudiness on adding silver nitrate. This cloudiness is probably due to hydrolysis of the salt. The analysee of barium salts prepared in this way, verify this supposition.

The analyses of two samples which were washed twice after filtering gave the following results:

			Found
I.	.1527 gm. salt gave .0454 gm. $BaSO_4$	Ba =	17.5
II.	.1041 " " " .0284 " $BaSO_4$	Ba =	16.6

Two samples washed until the cloudiness in the filtrate treated with silver nitrate did not diminish, gave the following results:

I. .1009 gm. salt gave .0263 gm. $BaSO_4$

II. .1124 " " " .0295 " $BaSO_4$

Calculated for $(C_{17}H_{23}O_2)_2 . Ba . (C_{17}H_{24}O_2)$		Found	
		I.	II.
Ba = 15.01	Ba =	15.31	15.45

This shows the formation of the acid salt.

From these results it would appear that there are two barium salts, the normal salt, obtained by neutralizing the acid in alcohol,

precipitating immediately by the addition of carbon dioxide free water and filtering as rapidly as possible; the acid salt obtained by precipitation from a weak alcoholic solution of the ammonium salt by the addition of barium chloride:

Calcium Betate, $(C_{17}H_{23}O_2)_2Ca$.- The calcium salt of betic acid is similar to the barium salt in the general properties. It was prepared by the same methods used in the preparation of the barium salt. However, it was not as granular and was therefore more easily precipitated and filtered from the alcoholic solution in which it was formed by titration with standard calcium hydroxide solution. Analyses of four different samples obtained by this method gave the following results:

I. .1058 gm. salt gave .0266 gm. $CaSO_4$

II. .0821 " " " .0212 " "

III. .0979 " " " .0234 " "

IV. .1118 " " " .0261 " "

Calculated for $(C_{17}H_{23}O_2)_2$.Ca		Found				
		I	II	III	IV	Aver.
Ca = 7.15	Ca =	7.228	7.597	7.031	6.868	7.181

The salts obtained by the addition of calcium chloride to the weak alcoholic solution of the ammonium salt, gave results which indicate that the normal calcium salt also hydrolyzes, forming an acid salt. In the preparation of this salt it was also impossible to wash the salt until the filtrate gave no cloudiness with silver nitrate.

The following analyses were made on two samples prepared in this way but not thoroughly washed:

I. .0643 gm. of the salt gave .0143 gm. $CaSO_4$

II. .0555 " " " " " .0119 " "

III. .0813 " " " " " .0171 " "

IV. .0730 " " " " " .0151 " "

Calculated for $(C_{17}H_{23}O_2)_2.Ca.\ 1/4\ C_{17}H_{24}O_2$ Found

I. II. III. IV. Aver.

Ca = 6.421 Ca = 6.54 6.306 6.25 6.26 6.339

Three samples prepared and washed until the cloudiness of the wash water did not diminish on addition of the silver nitrate, gave the following results:

I. .0537 gm. of the salt gave .0097 gm. $CaSO_4$

II. .1012 " " " " " .0180 " "

III. .0957 " " " " " .0163 " "

IV. .0843 " " " " " .0133 " "

V. .06755" " " " " .0102 " "

Calculated for $(C_{17}H_{23}O_2)_2.\ Ca.(C_{17}H_{24}O_2)$ Found

I. II. III. IV. V. Aver.

Ca = 4.878 Ca = 5.32 5.234 5.01 4.641 4.443 4.929

On washing a calcium salt prepared in this way several times beyond the point where cloudiness remained constant, the calcium was further reduced as indicated by the following determination:

.0854 gm. salt gave .0124 gm. $CaSO_4$ Ca = 4.271

It is evident from the above analyses that the calcium salt hydrolyzes more readily than the barium salt.

The Action of Ammonia upon Betic Acid.- The effect of dilute ammonium hydroxide upon betic acid was peculiar. The acid dissolved very readily and on standing or on warming to evaporate off the excess of ammonia and then cooling, the whole mass became a thick, stiff jelly. In the preparation of the barium and calcium betate, it was found necessary to get rid of this jelly by first dissolving it in about half its volume of 95 per cent. alcohol before adding the barium and calcium chlorides. Without doubt ammonia forms with the acid ammonium betate and the fact that barium and calcium more readily form the respective salts from the ammonia solution may be explained by the following equations:

$2\ C_{17}H_{23}O_2NH_4 + BaCl_2 = (C_{17}H_{23}O_2)\ Ba + 2\ NH_4Cl$ and

$2\ C_{17}H_{23}O_2NH_4 + CaCl_2 = (C_{17}H_{23}O_2)_2Ca + 2\ NH_4Cl$

On evaporating off the excess of ammonia from the ammonium hydroxide solution, a white powder was precipitated. Some of this white substance was filtered rapidly, dried in a vacuum dessicator over sulphuric acid for three hours and then analyzed for nitrogen. No nitrogen was found. Again, some of the undried white powder was dissolved in 62 per cent. alcohol and allowed to evaporate spontaneously. Crystals of the acid were obtained. Finally, the acid was dissolved in a small amount of ammonium hydroxide and the gelatinous ammonium salt allowed to evaporate to dryness in a vacuum dessicator over calcium chloride. Analysis of the dried substance gave no nitrogen. It was likewise dissolved in 62 per cent.alcohol, and again crystals of the acid were obtained. Attempts to determine the neutral

equivalent with ammonia failed as the acid was too weak to act upon congo red or any of the common indicators sensitive to ammonia.

Attempts were again made to precipitate the ammonium salt from a solution of the acid in organic solvents, by passing anhydrous ammonia into the solution (Jour.Am.Chem. Soc., 31,561). Ether was tried but no precipitate could be obtained. Acetone gave no better results. On passing the ammonia for a short time into a benzene solution, it suddenly solidified or jellified, similar to the ammonium hydroxide solution. A mixture of ether and benzene was then tried and gave promising results.

All of the experiments made thus far on the salts show that the acid is very weak, too weak in fact to act upon congo red, although strong enough to permit of titration with phenolphthalein as an indicator. It forms both normal and acid salts, hydrolyzing and changing from one to the other with water.

Hydrolysis was further proved by the action of the barium and calcium salts in different solvents. The salts used were those obtained by titration and precipitation with water. Their solubilities were similar, both dissolving in chloroform, glacial acetic, and alcohol. But in ether, benzene and acetone they seemed to dissolve at first, almost entirely, then to deposit an almost colorless mass, which, on filtering, drying and incinerating, proved to be only inorganic matter. It is evident, therefore, that these salts are slowly hydrolyzed even in benzene and acetone solutions, the acid dissolving and leaving the metallic salts, presumably the hydroxides or the carbonates, behind.

The Action of the Halogens on Betic Acid.- Iodine is rapidly absorbed by betic acid, forming well characterized compounds. These reactions are analogous to the common reactions known as the iodine and bromine absorption tests. The iodine value was therefore determined similar to the determination of the iodine values of the oils. Three absorption determinations gave the following:

	I	II	III	Calculated for
Wt. of acid	.20805	.20195	.2014	$(C_{17}H_{24}O_2)_2I_6$
I absorbed	118.4	116.8	117.1	122.1 o/o

The chloroform solution of the iodine compound was separated from the acid solution and allowed to evaporate spontaneously, forming a dark, reddish-brown, sticky mass, soluble in alcohol, and precipitated as an amorphous powder on the addition of water.

That the action of bromine on the acid might be studied, bromine was dissolved in chloroform and the acid added in the powdered form. Energetic action immediately followed the addition of the acid, liberating hydrobromic acid. The acid was added slowly until the vigorous action ceased. The chloroform was then allowed to evaporate spontaneously, when there remained a dark, thick, sticky mass, together with a small quantity of a light brown liquid having a pleasant odor. The liquid was poured off and the thick substance dissolved in the alcohol and water added until the solution became milky. On allowing the alcohol to evaporate spontaneously, the substance crystallized out. The substance recrystallized twice from alcohol, was of a light yellow color. It began to shrink at 98°, at 108° became clear and resinous and finally

melted at 119°-20°. At 134° it decomposed and at 178°-180° it was completely decomposed.

The analyses of two samples of the substances gave the following results:

I. .1655 gm. of the dry recrystallized substance gave .1118 gm.AgBr

II. .2088 " " " " " " " .1432 " "

Calculated for	Found	
$(C_{17}H_{24}O_2)_3 Br_4$	I.	II.
Br = 29.09	28.75	29.18

Mach(Monatsh.Chem.13, 627) claimed to have prepared a glycerine ester of abietic acid by allowing the acid and glycerine to stand in absolute alcohol for a long time. This experiment was repeated with betic acid except that the mixture was at first kept warm for about two hours and then set aside, loosely covered. On spontaneous evaporation of the alcohol, a light yellow crystalline substance was obtained, not resembling the acid in crystal form nor in melting point. Some of the substance was removed, pressed out on a porous plate to remove as much of the glycerine as possible, powdered, washed three times with a small amount of water, free from carbon dioxide, dried on a porous plate, and its melting point taken. On heating slowly, the substance began to shrink at 86°-87°, turning lighter in color. At 97° it became waxy and finally melted at 123°. However, on heating rapidly, it appeared to melt at 98°-99°.

The analyses of two samples of the substance, obtained in this way, gave the following results:

I. .1911 gm. of the dry substance gave .4989 gm. CO_2 and .1576 gm. H_2O

II. .1468 " " " " " " .3855 " " " .1240 " "

Calculated for	Found	
$C_{17}H_{23}O\cdot OH_2C\cdot CH_3(OH)_2$	I.	II.
C = 71.85	71.19	71.61
H = 8.98	9.10	9.38

These results indicate that a glycerine ester is formed by treating the acid in the above manner, one molecule of the acid combining with one molecule of glycerine, one molecule of water being split off.

Pitch.- To determine whether betic acid, which was obtained from resin that had been extracted from dry wood, existed as such in the original wood pitch. Experiments were started upon the pitch, which had been obtained by boxing. It was subjected to steam distillation to remove the terpanes. The residue was a clear, viscous, homogeneous liquid containing no visible crystals. This was extracted several times with warm 62 per cent. alcohol until a very small percentage of the original material remained undissolved. Upon allowing each separate fraction to stand, a liquid substance was deposited in every case, no crystals being obtained. After this non-volatile residue had stood for several weeks, crystals began to appear on the top of it and gradually spread down through it.

Fractional distillation at reduced pressure was tried, as being a possible method of isolating the chief acid of the pitch, or the substance from which it is derived. Fractions were collected every ten or fifteen degrees above 100°, the pressure varying from 50 to

60 millimeters. It was impossible to obtain a pressure lower than 50 millimeters. The temperature did not become constant until it had reached 260°, rising gradually to that point. Between 260° and 265°, at a pressure of 52 - 55 millimeters, a large amount of distillate was collected in five portions. The fourth portion distilled at 52 m.m., at a constant temperature of 260°. All of these were doubtless the same substance, the change in temperature being due to superheating, and to slight changes in pressure.

Four analyses made immediately upon the fraction distilling at 260° and 52 m.m. gave the following results:

I. .4026 gm. of the substance gave 1.2115 gms. CO_2 and .3693 gm. H_2O

II. .43485 " " " " " 1.2969 " " " .3942 " "

III. .3895 " " " " " 1.15895 " " " .3481 " "

IV. .3580 " " " " " 1.0407 " " " .3118 " "

Calculated for		Found			
$C_{34}H_{52}O_3$		I.	II.	III.	IV.
C =	80.31	82.06	81.33	81.14	79.28
H =	10.23	10.19	10.07	9.93	9.72

These analyses show that a change was taking place in the substance, probably due to oxidation, since the carbon and hydrogen both decrease in about the same ratio, indicating an absorption of oxygen. When first distilled the substance was very viscous. It had a golden yellow color, which changed to a deep orange-yellow on standing exposed to the light. If the substance was kept in the dark only a very slight change in color was noticed after several months. It is evident that light has some effect upon the substance, as will be shown below. No crystals could be obtained from the alcohol ex-

tract of the freshly distilled material.

Upon allowing the distillate analyzed above to stand for over a month, crystals appeared on the top of the substance and on the sides of the containing vessel where there were thin layers of the material. It was found, on stirring these into the substance, that more crystals were obtained. Stirring of the other portions distilling between 260° and 265° gave crystals. With occasional stirring during a period of nearly two weeks, the whole mass was filled with crystals suspended in the thick,viscous substance. This material was extracted with 62 per cent. alcohol. The extract deposited beautiful white crystals resembling those of betic acid. Fractional recrystallization gave two distinct substances. That which crystallized out first melted at 143° to 144°, indicating betic acid. The substance which crystallized last had a melting point of 156° to 157°. Two recrystallizations of this substance failed to change the melting point. This acid is probably the same as that obtained by Rabak(Pharm.Review,1904, 293) from Oregon balsam, better known as Douglas Fir. He obtained from glacial acetic acid solution an acid melting at 156° to 157°. A second crop of crystals, melting at 143°, was obtained. This acid may be identical with betic acid. The melting point of both acids, determined a year later, had lowered to 147-148° and 131-132° respectively, showing that the acid, even in the crystallized form, undergoes a change when exposed to the air.

It is worthy of note that crystals could not be obtained from a fraction of another distillation collected under the same conditions as the above, but allowed to stand in the light. It is possible that a different process of oxidation takes place in the light than in the dark.

Three analyses upon this crystalline acid gave the following results:

I. .1687.gm. of the dry substance gave .4579 gm. CO_2 and .1444 gm.H_2O

II. .1763 " " " " " " .4822 " " " .1521 " "

III. .1783 " " " " " " .4833 " " " .1509 " "

Calculated for	Found		
$C_{17}H_{26}O_3$	I.	II.	III.
C = 73.38	74.03	74.53	73.92
H = 9.35	9.51	9.58	9.40

After the crystals had been extracted from the above mass, a viscous liquid remained from which crystals could not be obtained. This was subjected to fractional distillation at 60 m.m. pressure. An analysis of the distillate collected between 248° and 254° gave the following results: .3213 gm. of the substance gave.9647 gm.CO_2 and .2998 gm. H_2O.

Found C = 81.88 : H = 10.37

An analysis of the distillate collected between 254° and 262° gave the following results:

.3143 gm. of the substance gave .9288 gm. CO_2 and .2853 gm. H_2O.

Found C = 80.60 : H = 10.09

These analyses agree fairly well with those of the distillate above from which the crystals were obtained, indicating that it is the same substance. This was some of the last work completed so there has not been opportunity to investigate the possibility of obtaining crystals from this distillate. Further work will be done upon it.

The results obtained from work upon the pitch indicate that in the process of alteration there occurs a compound having the composition represented by the empirical formula $C_{34}H_{52}O_3$. This is a thick, viscous substance which readily absorbs oxygen from the air, going over into a crystalline substance, the composition of which may be represented by the formula $C_{17}H_{26}O_3$ or $C_{34}H_{52}O_6$. This change would be represented by the following equation: $2\ C_{34}H_{52}O_3 + 3\ O_2 = 4\ C_{17}H_{26}O_3$ or $2\ C_{34}H_{52}O_6$.

Betic acid can be considered to be derived from this crystalline compound by hydrolysis, as represented by the following equation: $C_{17}H_{26}O_3 - H_2O = C_{17}H_{24}O_2$.

From the above facts one may draw the conclusion that the principal acid in the resin of the Douglas Fir is betic acid; a new acid having the formula $C_{17}H_{24}O_2$. It may be considered to be formed from a substance having the composition represented by the empirical formula $C_{34}H_{52}O_3$, first by oxidation to $C_{17}H_{26}O_3$, and then by dehydration of this substance. While the analysis of betic acid is not far from that given for japopinic, canadinic and picipimaric acids, it differs greatly from them in physical and chemical properties.